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Friday November 6th 2009

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Dear Sir,

I hereby submit my Thesis titled "Characterization of Nickel Hydroxide "Gel"" for consideration as partial fulfillment of the Bachelor of Engineering degree.

All the work contained within this Thesis is my original work except where otherwise acknowledged.

I understand that this thesis may be made publicly available and reproduced by the University of Queensland unless a limited term embargo on publication has been negotiated with a sponsor.

Yours sincerely

William John Hawker
Student ID: *41187940*

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Extended Abstract

Precipitation of nickel and cobalt as a mixed hydroxide is an increasingly popular step used to produce an intermediate product in the processing of laterite ores. The main constituent of the precipitate is nickel at approximately 50% of the solid w/w. The industrial precipitation of the mixed hydroxide is carried out with seeding and at elevated temperatures (50°C) to ensure a filterable precipitate forms. Research was carried out last year at UQ investigating methods of improving the quality of the precipitate product. An observation was that at room temperature the mixed hydroxide precipitates as a voluminous green gel-like suspension.

The aim of this thesis was to investigate the formation and properties of hydroxide "gels", specifically focusing on nickel with mind to understanding the chemical, physical and thermodynamic properties of the "gel" and mixed hydroxide systems in general. This will be achieved by:

- Collating the current knowledge regarding nickel hydroxide and gel-like precipitates and the factors affecting their formation
- Experimentally defining the physical, chemical and thermodynamic properties of the nickel hydroxide gel-like precipitates and investigating the factors affecting their formation
- Providing scoping and ground work for further research

Industrial mixed hydroxide precipitation is carried out in aqueous sulphate systems, so the scope of this investigation was limited to studying these simplified industry analogous systems. Literature pertaining to the nickel hydroxide "gel" is minimal, as previous research focuses on either the α- or β-phase crystalline precipitate in relation to its use in batteries. The α-phase is an irregularly layered, highly hydrated precipitate which is believed to decompose into the well orientated and layered precipitate β-phase over time as the impurities are slowly occluded by the crystal structure.

This study proposes that the nickel hydroxide "gel" precipitated at room temperature forms an amorphous, highly hydrated gel as defined by Stokes and Frith (2008) when in solution and once filtered it dehydrates to form a vitreous or glassy solid with no long range atomic structure. Calculations on the energy of formation for the amorphous precipitate show that it is less stable that crystalline nickel hydroxide with its energy of formation at -443.2 ±2.0 kJ/mol as opposed to

crystalline form at -453 kJ/mol. This indicates that the amorphous precipitate is a metastable phase with the crystalline form thermodynamically favourable but not achievable due to energy constrains. Equilibrium experiments showed that nickel hydroxide precipitates with between 10 and 25% less than the stoichiometrically required amount of hydroxide however, month long experiments found the precipitate began to absorb in more hydroxide over time. Therefore the system was not fixed at a chemical equilibrium and may have been morph rearranging into the crystalline phase over the experimental time frame.

Other precipitation system components significantly affected the precipitation thermodynamics of the amorphous precipitate. When separate, cobalt hydroxide will form at a slightly higher pH to nickel hydroxide but when cobalt is included in the nickel hydroxide precipitation system, the cobalt is stabilised to the solid phase at much lower pH values. When the nickel and cobalt hydroxide precipitate was filtered, it formed a cake approximately 3 times larger than the combined volume of the individual nickel and cobalt hydroxide precipitates.

Within the aqueous sulphate system the amorphous nickel hydroxide has a hydration factor of approximately 200-300 water molecules per nickel hydroxide molecule. Once it is filtered the hydration drops to approximately 25 water molecules per nickel hydroxide molecule. Over time the filtered precipitate dehydrated further. When the dry cake was submerged in distilled water it was observed to shatter and eject shards approximately 1mm diameter within the space of two minutes.

Further research has also been proposed:

- Longer term experiments are required to prove whether the amorphous precipitate was in fact decomposing into a more crystalline structure or simply shifting around within the bounds of the metastable phase.
- XRD analysis is required to prove that the filtered precipitate is in a glassy state with no long range crystal structure.
- Analysis on the gel inclusions is required to gain a greater understanding of the stability of different species within the gel and the attractive and repulsive forces during the formation of the gel

Contents

Tables

Figures

Equations

Definitions

coll · oid · al · · state – noun

A system of particles in a dispersion medium in which particles are between 10^-5 and 10^-7 cm i.e. between a true molecular solution and a coarse suspension.

(*The Macquarie Dictionary* 1982, p. 367)

crys · tal – noun

A solid body having a characteristic internal structure and enclosed by symmetrically arranged plane surfaces, intersecting at definite and characteristic angles.

(*The Macquarie Dictionary* 1982, p. 452)

crys · tall · ite – noun

A minute body in igneous rocks marking an incipient stage in crystallisation.

(*The Macquarie Dictionary* 1982, p. 452)

gel – noun

A semirigid colloidal dispersion of a solid with a liquid or gas, as jelly, glue or silica gel.

(*The Macquarie Dictionary* 1982, p. 742)

plate · let – noun

A microscopic disc occurring in profusion in the blood, and acting as an important aid in coagulation.

(*The Macquarie Dictionary* 1982, p. 1325)

1. Introduction

One method of processing nickel laterite ore is a hydrometallurgical route employing a strong acid leach. The ore is usually leached at high temperature and pressure using sulphuric acid. The leach solution, containing a number of dissolved metals, is then separated from the residue and metals are selectively precipitated by pH adjustment. The pH adjustment can be carried out using sulphide, carbonate or hydroxide reagents which form the respective metal bonded precipitates. Sulphide and hydroxide reagents will often co-precipitate any cobalt from solution, forming an important secondary product from the laterite ore bodies.

The industrial precipitation of nickel hydroxide is carried out with seeding and at elevated temperatures (50°C) to ensure a filterable precipitate forms. Research carried out by Robin Harvey at the University of Queensland last year found that when the nickel hydroxide precipitation is carried out at room temperature without seeding, the resulting nickel hydroxide forms a gel-like precipitate

1.1 Context

In current industry practice the formation of any gel-like precipitate is avoided as the fine precipitate particles cause significant handling and processing difficulties. There is a significant lack of knowledge regarding the nickel hydroxide gel-like precipitate due to this avoidance. There may be properties of the gel-like precipitate that are advantageous and could be employed to improve the extraction process.

1.2 Objective

This thesis aims to provide a positive contribution to literature by:

- Collating the current knowledge regarding nickel hydroxide and gel-like precipitates and the factors affecting their formation
- Experimentally defining the physical, chemical and thermodynamic properties of the nickel hydroxide gel-like precipitates and investigating the factors affecting their formation
- Providing scoping and ground work for further research

1.3 Scope

Due to the nature of this particularly exploratory task, the scope of the project is wider rather than deeper in order to broaden the current information base regarding nickel processing and hydroxide precipitation.

Experimentally, the scope of this investigation is limited to studying nickel hydroxide precipitated from sulphate systems. This corresponds with the industry practice of sulphuric acid leaching followed by hydroxide precipitation. These aqueous systems will be synthesised simplistically to remove most or all of possible contaminants although the effect of some of the important and interesting leach solution constituents will be included in the experimentation. The precipitation experiments will only be carried out using sodium hydroxide as the precipitation agent in order to simplify the calculations.

1.4 Outline

A literature review was carried out in order to gain an understanding of the chemistry and thermodynamics involved in the nickel hydroxide precipitation. Areas where the current knowledge of gelatinous nickel hydroxide was lacking were used to derive hypotheses for the experimental scope. A project risk analysis and some initial laboratory testing provided the foundations to design experiments and develop a suitable methodology and set-up with which to investigate the hypotheses. The system and precipitate characteristics are discussed with respect to the hypotheses made. Finally, unresolved issues and ideas generated from this thesis are recommended for further research and interpretation.

2. Literature Review

This literature review aims to collate the current knowledge regarding the nickel hydroxide gel-like precipitate and the factors affecting its formation.

This literature review casts a wide net over both nickel and the hydroxide precipitation process. The relevant factors regarding precipitation chemistry with respect to nickel hydroxide precipitation and crystallisation are investigated. The formation and processing of nickel laterite ores has been investigated to gain an appreciation of the hydrometallurgy and associated issues.

2.1 Precipitation Chemistry

Precipitation occurs when the concentration of a solute exceeds the solubility value of that particular solute, i.e. the solution is supersaturated (Sist 2004, p. 41). Precipitation is a process involving nucleation and growth. Nucleation is defined as the formation of a stable nucleus, whether onto an existing surface by primary heterogeneous nucleation or as a new individual particle by primary homogeneous nucleation. Nucleation can also occur as secondary nucleation, where a new nucleus is created from a larger particle. Table 1 classifies the nucleation mechanisms (Harvey 2008, pp. 32-3).

Table 1 - Classification of Nucleation Mechanisms

Primary Nucleation	Secondary Nucleation
Heterogeneous Homogeneous	Contact Shear Fracture Attrition

2.1.1 Supersaturation

The nucleation and growth mechanisms which make up precipitation are driven by the degree of supersaturation of the precipitating species. The degree of supersaturation is defined as the concentration fraction in excess of the equilibrium saturation concentration at the relevant solution temperature and pH conditions (Harvey 2008, p. 33). The degree of supersaturation is represented by Equation 1.

Equation 1 - Degree of Supersaturation

$$SS = \frac{C_{actual}}{C_{equilibrium}}$$

The degree of supersaturation only applies when the actual concentration of the solute is greater than the equilibrium concentration of the solute. If the actual concentration is less than the equilibrium concentration, then the solvent is not saturated and precipitation will occur and any precipitate should dissolve into solution. If the actual concentration is at the equilibrium concentration, the solution is at saturation and the supersaturation is equal to 1. The system will be in equilibrium between precipitation and dissolution. When the degree of supersaturation is greater than 1, nucleation and growth can occur. Primarily heterogeneous precipitation and growth will dominate homogenous nucleation unless the solution is above a certain critical degree of supersaturation. (Sist 2004, p. 50)

If the concentration is higher than the supersaturation level at which homogenous precipitation will occur, precipitates tend to be in an amorphous phase which is less stable, more difficult to filter and contain higher concentrations of impurities. (Sist 2004, p. 50)

2.1.2 Heterogeneous Precipitation

Heterogeneous precipitation occurs when impurities or active surfaces are included in the system. The solute precipitates by forming nuclei on the impurities or active surfaces. Impurities can significantly affect the rate of nucleation of a solution. They can act as either nucleation accelerators by providing active surfaces or appropriate lattice structures, or they can act as nucleation inhibitors by deactivating surfaces. (Mullin 2001, p. 192)

Secondary nucleation is distinguished from primary nucleation because secondary nucleation occurs when crystals of the solute are already present within the solution. Secondary nucleation can occur by attrition, fracture or shearing forces which create new nuclei from the existing particles. Contact nucleation is defined as nucleation on an existing particle of the particular solute where the existing particle looses its original shape. (Harvey 2008, p. 33)

2.1.3 Homogeneous Precipitation

Homogeneous nucleation occurs when nuclei are formed spontaneously within the solution. It is usually undesirable in commercial precipitation because it tends to form fine, poorly crystalline

precipitates (Harvey 2008, p. 33). The exact process by which a stable nucleus is formed within a homogeneous fluid without the aid of an active surface of impurity on which to nucleate is not understood completely. It has been likened to the example of the condensation of a supersaturated vapour to become liquid. This process is only possible with the appearance of microscopic droplets, called condensation nuclei, on the condensing surface. These condensation nuclei do form but the vapour pressure at the surface of these miniscule droplets is incredibly high which means they evaporate rapidly even when the surrounding vapour is supersaturated. Over time new nuclei form while old ones evaporate, until stable droplets are formed either by coagulation of the condensation nuclei or under conditions of significantly higher vapour supersaturation caused by incomplete mixing. The formation of crystal nuclei is even more complicated than this because not only do the constituent molecules have to coagulate in sufficient numbers through a much more dense medium, usually they also have to become orientated into the particular lattice structure being formed. The number of molecules required to form a stable nucleus can vary from about ten to several thousand, for example ice nuclei may contain about 100 water molecules. However, the stable nuclei are not expected to be resultant from the simultaneous collision of the required number of molecules as this would be an incredibly rare event. Rather it is expected to arise from a sequence of bimolecular additions according to Equation 2.(Mullin 2001, p. 182)

Equation 2 - Proposed nuclei formation equations

$$A + A = A_2$$
$$A_2 + A = A_3$$
$$A_{n-1} + A = A_n$$

Where n is the number of molecules required to form the stable nuclei. (Mullin 2001, p. 182)

The nucleus is very unstable at low supersaturation levels so homogeneous precipitation only occurs in regions of very high supersaturation (Sawada 1998).

This proposed mechanism of nucleus formation highlights the blur in definitions between nucleation and growth because further addition of molecules to this A_n nucleus is labelled as growth of the nucleus even though the A_n nucleus is not properly defined in all possible cases.

2.1.4 Growth

Particle growth is where precipitation occurs onto existing nuclei or particles in such a way that the nucleus or particle retains its mother shape (Harvey 2008, p. 33). This will usually occur in preference to the primary nucleation of new particles due to thermodynamics, although growth obviously requires the presence of nuclei to provide the growing surface. Growth occurs due to the combined effect of diffusion and surface adsorption. (Mullin 2001)

In a batch aqueous system, once the solute concentration is increased above the equilibrium concentration and reaches the concentration corresponding to critical supersaturation, homogenous nucleation will occur until the solute concentration reaches the minimum supersaturation for spontaneous nucleation. The solubility equilibrium will then be achieved by growth processes. (Sist 2004, p. 46)

One method of enforcing only heterogeneous precipitation is to employ a step-wise neutralisation process. In this process, the solution is neutralised by slowly adding base until the pH specified at point 1 is reached. This pH is less than the critical concentration at which homogenous precipitation will occur although it is greater than the equilibrium or saturation concentration. The solution is then given time to equilibrate which will cause the precipitation of, in the case of a nickel solution, nickel hydroxide. This heterogeneous precipitation process can be hastened by the addition of seeds of excess free surfaces. As the nickel precipitates, its concentration will decrease until equilibrium is reached. At this point, more base is added to carry out another step and form more heterogeneously precipitated nickel hydroxide. (Sist 2004, p. 51)

2.1.5 Solubility and Equilibrium

For the purpose of this thesis, it is assumed that the the activity of a species is equal to the concentration of the species, although methods of calculating the activity without this assumption have been investigated.

It has already been mentioned that precipitation will only occur when the concentration of a particular solute exceeds its own solubility value. The solubility value is often expressed as the concentration solubility product, but this value is only applicable in simple cases where the solute is a sparingly soluble electrolyte in water or very low concentrations are expected. Looking at the simplest case, if one molecule of the sparingly soluble electrolyte in water dissociates in solution into x cations and y anions, the reaction occurs according to Equation 3.

Equation 3 – General electrolyte dissociation reaction

$$M_x A_y \leftrightarrow xM^{z+} + yA^{z-}$$

Then for the saturated solution solubility can be expressed by Equation 4.

Equation 4 – Saturated solution concentration solubility for an electrolyte

$$(c+)^x (c-)^y = constant = K_c$$

Where c+ and c- are the ionic concentrations expressed in moles per L.

For a salt which produces two ions per molecule, one cation and one anion, Equation 5 applies.

Equation 5 – Saturated concentration of one cation one anion electrolyte

$$c+ = c- = c^*$$

Where c* is the equilibrium solubility in moles per L

Therefore the saturated solution equilibrates to give Equation 6.

Equation 6 – Saturation solubility concentration of one cation one anion electrolyte

$$c^* = K_c^{\frac{1}{2}}$$

The general equation is given in Equation 7.

Equation 7 – General concentration saturated solubility for an electrolyte

$$c^* = \left(\frac{K_c}{x^x y^y} \right)^{\frac{1}{x+y}}$$

However, the simple concentration solubility product principle has very limited use. For more concentrated solutions the fundamentals of activity must be taken into account.

The activity solubility product is defined by Equation 8

Equation 8 - Saturated solution activity solubility

$$(a+)^x (a-)^y = constant = K_a$$

The activity of an ion may be expressed in terms of the ionic concentration, c, and the ionic activity coefficient, γ. Therefore Equation 8 simplifies to Equation 9.

Equation 9 - Saturated solution activity solubility in terms of ionic concentrations and activity coefficients

$$K_a = cons\tan t = (c+\gamma+)^x (c-\gamma-)^y$$

And further simplifies to Equation 10.

Equation 10 - Saturated solution activity solubility in terms of mean activity coefficient

$$K_a = K_c(\gamma\pm)^v$$

Where ɣ± is the mean activity coefficient and v= x+y, the number of moles of ions produced by one mole of electrolyte.(Mullin 2001, pp. 104-5)

2.1.6 **Activity**

As noted in the previous section, the concentration based solubility is only applicable in certain situations. One method of calculating the activity of a species was developed by Meissner although interpreting and undertaking the calculations is deemed outside the scope of this thesis.

2.1.7 **Free Energy**

Precipitation occurs through the processes of nucleation and growth but in effect, the occurrence of precipitation all comes down to the system thermodynamics. The second law of thermodynamics effectively states that precipitation will occur if the free energy change of the precipitation reaction is less than zero. Further, equilibrium is achieved when the free energy of the precipitation reaction is equal to zero and the precipitate will dissolve if the free energy of the precipitation reaction is greater than zero. The relationship between the free energy of a reaction and the reaction equilibrium constant is described in Equation 11.

Equation 11 - Free energy of reaction relation to the reaction equilibrium constant

$$\Delta G_{rxn} = -RT\ln(K_{rxn})$$

The free energy of the reaction at standard conditions (25 degrees C, 1atm) is calculated by Equation 12.

Equation 12 - Free energy of a reaction at standard state

$$\Delta G^0_{rxn} = \sum \Delta G^0 products - \sum \Delta G^0 reac\tan ts$$

When the system is not at standard conditions, the equations must be modified using correction factors.

2.1.8 Temperature Effects

The temperature of operation significantly affects the precipitation of a solute because the solubility is temperature dependant. At the thermodynamics level, the free energy of the precipitation reaction is affected by the temperature which is related to the solubility. The temperature of the solution will also affect the kinetics of any reactions because a hot solution is effectively at a higher energy state.

2.1.9 Surface Energy

The surface energy of a particle is known to have a significant effect on its solubility. Fine solids have a greater solubility than large crystals because the fine particles have a higher surface tension. But smaller particles will also have a faster rate of solution per unit of surface area because they have a higher surface energy. (Enustun & Turkevich 1959)

Enustun & Turkevich (1959) carried out a number of experiments investigating the relationship between solubility and particle size. One experiment was carried out measuring the solubility of a solution equilibrated with fine particles which then had large particles added. The solubility of the precipitate was not affected by the large particle addition. They carried out the same experiment equilibrating a solution with large particles then adding fine particles. The solubility of the precipitate increased significantly. They concluded that the solubility of the solubility of a species within a solution was only related to the solubility of the finest particles in the solution. This is a significant fact and must be taken into account when analysing the nickel hydroxide precipitate. It may also have significant repercussions on the way which seeding and secondary nucleation are understood.

2.1.10 Metastable Precipitation

In crystallization processes it is not uncommon for the first visible crystalline phase to be a metastable polymorph or hydrate. This fits with Ostwald's rule of stages where he states that: an unstable system does not necessarily transform into the most stable state, but into one which most closely resembles its own, i.e. into another transient state whose formation from the

original represents the smallest loss of free energy. Some metastable phases rapidly transform to a more stable phase while others can exhibit apparent stability for a very long time. Some transformations are reversible (enantiotropic) while others are irreversible (monotripic). In some cases the metastable phase may have more desirable properties than the stable phase, and in these cases it is important to isolate and dry it quickly to prevent it from transforming to the stable form. Once in the dry form, a metastable form can often remain unchanged indefinitely.

Because polymorphs have different lattice structure or different spacing of lattice points, they may often be readily identified by visual or microscopic observation. Strictly speaking, hydrates are not polymorphs because they are chemically different from their parent compounds although the still have the characteristics such as the ability to transform to more stable forms. Polymorphs and solvates can be identified and characterised by several analytical techniques such as powder X-ray diffraction, IR and NMR spectroscopy and TGA, thermogravimetric analysis. (Mullin 2001, pp. 214, 80-81)

2.1.1 Soft Matter

Soft matter is a rheological term that refers to structured fluids that respond strongly to applied stress. The soft matter behaves in a solid-like fashion when little to no stress is applied but above a critical stress values the solid flows or yields in a solid-to-fluid transition. Soft matter is most often encountered in everyday life in the form of household consumer products such as toothpaste, detergent, tomato sauce, mayonnaise, shampoo & cosmetics. Other examples include biological species such as tissues, cells and blood and importantly from a metallurgical sense, geological species such as mud and sediments. These soft matter systems are highly complex rheologically and contain hierarchical metastable structures that range in size from macro to nano scale. (Stokes & Frith 2008)

Soft matter often contains multiple phases on the micro or nano scale such as particles, liquid droplets and or air suspended within the overall soft matter phase. Consumer products are often designed and assembled with structurants in order to ensure the long term stability of the soft matter and minimise the effect of any variations in temperature, pressure and shearing conditions that the product may undergo. (Stokes & Frith 2008)

The stability of many of these soft matter systems is dependent on the structure formation and rheology at the air-liquid and/or liquid-liquid interface during formation. For example, the

formation of an elastic or rigid interface can be used to prevent coalescence and disproportionation of liquid and air droplets. (Stokes & Frith 2008)

A gel is generally considered to have a low volume fraction of structuring agent or dispersed phase, such that there is an interconnected network structure whereby it is considered to be a percolated solid, while a soft-glass consists of a disordered solid phase that is in a dynamically arrested state that occurs at high volume fraction of structurant or included phase that is considered 'soft'. However, it is not always clear whether a system is a gel or glass since the effective phase volume can be different than expected based on individual particle size due to surface forces, solvent conditions, hydration, swelling, etc. In addition, many soft matter systems contain elements of both a soft glass and gel; that is, a highly filled system that also includes an interconnected network of structural entities or included phase. Hence, the origin of soft matter rheology and the distinction between a glass and a gel for many systems is not always obvious from rheological measurements themselves, or through microstructural investigations. (Stokes & Frith 2008)

2.2 Aqueous Nickel Chemistry

Nickel is a group VIII (10) transition metal with the chemical symbol Ni and atomic number 28. While nickel cn achieve a number of oxidation states, the only one of interest to this thesis is also the form found in the majority of nickel compounds, Ni(II). (Cotton & Wilkinson 1988, pp. 724-55).

Ni(II) can form a large number of complexes with coordination numbers from 3 to 6. This leads to the existence of complicated equilibria which are temperature and concentration dependent and involve multiple structure types (Cotton & Wilkinson 1988).

The four-coordinate complexes of nickel are known to associate or polymerize to give species in which the nickel ions become five- or six-coordinate. The association between the six-coordinate polymer is very strong in some cases and the individual four-coordinate monomers are only observed at very high temperatures. Other four-coordinate complexes polymerize with weaker bonding such that the temperature and concentration dependent equilibrium is around room temperature. In these cases both the red diamagnetic monomers and green or blue paramagnetic polymers can be present. (Cotton & Wilkinson 1988, pp. 724-55)

The main molecule formed by the 6 coordinated nickel is the bright green octahedral hexaaquanickel complex $[Ni(H_2O)_6]^{2+}$. Some or all of the water molecules in this complex can be displaced by various neutral ligands. These complexes are characteristically blue or purple due to the shifts in the absorption bands when water ligands are replaced by others lying towards the stronger end of the spectrochemical series (Cotton & Wilkinson 1988, pp. 724-55).

$[Ni(H_2O)_6]^{2+}$ are immediately generated upon dissolution of simple Ni^{2+} salts in water containing non- or weakly coordinating counter-anions such as SO_4^{2-} (Cotton & Wilkinson 1988, pp. 724-55). While the $[Ni(H_2O)_6]^{2+}$ complex is accepted as the main molecule formed by aqueous nickel, the basis of a single shell of water molecules weakly surrounding the metal ion gives the impression that substitution of these water molecules is easy. This is not the case as the closest or primary shell of water molecules is actually somewhat removed from interaction with the bulk solution due to the existence of secondary and in some cases a tertiary shell. For interaction between ligands and the metal ion to take place, the ligand must effectively diffuse through tertiary and secondary solvation shells to then substitute into the primary solvation shell.

The degree of hydration and the rate at which substitution or exchange can occur for a given metal ion is determined by the metal ion's properties such as its ionic size and charge density. The ionic hydration enthalpy fits a linear relationship with decreasing size and increasing charge density. (Richens 1997, pp. 4-5)

The hydration enthalpy for each ion has a relation to the rate at which the ion can exchange complexed molecules. Exchange of the water on the $[Ni(H_2O)_6]^{2+}$ ion occurs with a rate 10^2 times slower than on the corresponding octahedral Fe2+ or Co2+ aqua ions. (Richens 1997, pp. 491-9)

2.2.1 **Nickel Hydroxide Crystallisation**

Nickel hydroxide may be precipitated from aqueous solutions of Ni(II) salts by addition of an alkali metal hydroxide such as NaOH. It tends to form a voluminous green gel. The gel crystallizes on prolonged storage. It is not amphoteric (Cotton & Wilkinson 1988, pp. 724-55). Amphoteric is defined as 'functioning as an acid or as a base' (*The Macquarie Dictionary* 1982, p. 100).

Nickel hydroxide is known to form a number of different crystal structures. The anhydrous β-phase has repeating, well-oriented unit structures while conversely the α-phase is hydroxyl deficient. The anhydrous β-$Ni(OH)_2$ is also known as the mineral theophrastite. It forms a structure where the hydroxide ions are hexagonally packed around nickel ions which are found on alternating rows of octahedral sites creating a layered structure (Sist 2004, p. 62).

The α-phase is hydroxyl deficient due to loosely bound hydroxyl anions substituting with impurity anions such as SO_4^{2-} in the interlayer region (Rajamathi & Kamath 1998). Due to the uptake of matrix anions and water impurities in the α-phase, the crystal structure exhibits larger interlayer spacing. The α-phase is typically hydrated and is represented by the formula in Equation 13. The weak interlayer bonding causes irregular orientation of layers and hence distortion of XRD patterns. (Harvey 2008, pp. 29-30)

Equation 13 - Typical α-Ni(OH)2 phase formula

$$Ni(OH)_{2-x}A^{n-}{}_{x/n}.mH_2O$$

Where A^{n-} = anion, x = 0.05 – 0.4, m = 0.6 -1

XRD patterns of precipitated nickel hydroxide may exhibit distortion and peak splitting due to mixed precipitation of α and β phases. This has been observed in nickel hydroxide precipitates formed at low pH (around 6) and low temperature values (around 65 °C) from simple, synthetic nickel and magnesium sulphate solutions (Sist & Demopoulos 2003).

Song et al. (2002) investigated the structural characteristics of nickel hydroxide precipitates. They found that the structural characteristics of the synthesized b-Ni(OH)2, such as degree of crystallinity, crystalline lattice disorders, crystallite size and crystal growth orientation were strongly related to the pH values of the chemical precipitation reaction. The amounts of SO_4^{2-}, CO_3^{2-} and H_2O adsorbed in crystals, and the thermal stability of the b-Ni(OH)2 also depended on the pH. Under relatively high pH values, the synthesized nickel hydroxide materials possessed a reduced crystallite size and lower thermal stability, more crystalline defects and a higher Ni composition. (Song et al. 2002)

A precipitation mechanism based on the minimal structural change principle has been proposed by Soler-Illia et al (1999). The minimal structural change principle, like Ostwald's rule of stages,

states that the coordinative environment of the aqueous species that initiate precipitation are those that resemble ions in the solid state. This proposed mechanism relies on the hexaaquanickel complex hydrolysing to form $NiOH^+$ ion which then condenses into the $Ni_2(OH)_2^{2+}$ monomer. Two monomers can bond to form the $Ni_4(OH)_4^{4+}$ tetramer which condenses when the correct steric arrangement is achieved to develop planes of nickel and hydroxide by expelling the excess hydroxide and rapidly form into platelets[1]. The plains rapidly develop; trapping any aqua molecules still held within the tetramer's hydration shell. Once the size of the polyion surpasses the critical nucleation value, subsequent growth proceeds by the addition of hydroxylated and complexed monomers. The crystallites[2] identified just before the onset of precipitation appear to be composed of seven nickel hydroxide layers with a basal dimension of ca. 19 nm, i.e. about 35 x 35 unit cells. (Soler-Illia et al. 1999)

Anions other than hydroxide also play a decisive role in homogenous precipitation of metal hydroxides. Some anions are strongly coordinated to the dissolved metal ions and thus end up in the precipitated solids at fixed stoichiometric composition. On other systems, co precipitated anions in monodispersed particles can be readily removed by leaching. (Matijevic 1985)

The phase interfaces involved in the precipitation will also affect the precipitation inclusions as the water region near an interface will incorporate or exclude ion species relative to the bulk solution in accord with the effect of these species on water structure. This is because the structure of liquid water is different near a gas-water, liquid-mater, or solid-water interface than in the bulk water. For example, the surface electrical conductivity of aqueous electrolytic solutions is less than the bulk conductivity due to enhanced water structure and/or ion exclusion. If there are charge sites on the surfaces of the pores, the situation will be further complicated by ion exclusion arising from the electric double layer. In a system of great surface area, such as a gel, where the amount of water near a surface is comparable to the amount distant from a surface, the effects of interface-produced disturbances on the concentration of ionic constituents should become appreciable. (Stokes & Frith 2008)

[1] See Definitions

[2] See Definitions

Achararya et al. (2003) carried out a number of experiments precipitating nickel hydroxide. They found that the percentage of nickel in nickel hydroxide samples precipitated with sodium hydroxide was only 51.5%, much less than the theoretical value of 63.4%. The hydration was 16.0% or approximately 1 water molecule per nickel hydroxide molecule. The mass due to intercalation of anions was found to be ~2.5%. The adsorbed anions were found to be SO_4^{2-}, CO_3^{2-}, HCO_3^- or NO_3^-. (Acharya et al. 2003) The presence of such species in the nickel hydroxide after thorough washing with distilled water has been reported by Baraldi et al. (1989). (Baraldi et al. 1989) .

Jayashree and Kamath (1999) suggest two methods by which inclusions can be intercalated into the structure of cobalt hydroxide without relying on simple hydroxide substitution:

1. By partial protonation of the hydroxyl groups
2. By partial substitution of an octahedrally co-ordinated cation by two tetrahedrally coordinated ions on either side of the octahedral vacancy

The first method may also apply to the precipitation of nickel hydroxide although the second cannot apply as the nickel ions cannot achieve an octahedrally co-ordinated state. Despite this, the two methods explain why β- nickel and cobalt hydroxides, which are not hydroxyl deficient, still include impurities.(Jayashree & Kamath 1999)

The various forms of $Ni(OH)_2$ differ from each other by their chemical structure, degree of hydration and morphology. The materials with a lack of crystallinity (Song et al. 2002), high specific area, high degree of porosity and low particle size are known to have better charge/discharge capacities and as such have superior electrochemical properties when compared to that prepared chemically. Thus, in contrast to the metallurgical industry, in the nickel hydroxide battery industry it is desirable to produce nickel hydroxide with these specific characteristics. The precipitation of nickel hydroxide in the presence of complexing reagents is one such method. A complexing agent essentially controls the kinetics of nickel hydroxide precipitation by fixing the free nickel ion concentration within the solution. (Subbaiah et al. 2003)

Throughout this discussion on nickel hydroxide phases and crystal structures, there is no clear definition distinguished in literature regarding size definition of the precipitated particles.

Because of this, it is not clear whether the literature is describing the precipitation of visibly crystalline particles or colloidal gels. The confusion is heightened by authors also describing their experimental results as "badly crystallised" β-phase precipitates or hydrated α-phase precipitate. The size of the precipitate is incredibly important to the processing viability of precipitates. Particle size distributions for MHP carried out by Oustadakis, Agatzini-Leonardou and Tsakiridis (2006) show the existence of MHP particles as fine as 100 nanometres. There may be particles smaller than this that were not taken into account due to the limitations of the sizing method. The finer MHP particles have already been described as very hard to filter and handle. (Oustadakis, Agatzini-Leonardou & Tsakiridis 2006)

The Macquarie Dictionary definition[3] outlines the size boundaries described in Table 2.

Table 2 - Particle size based classification of solution dispersions

	Molecular Solution	Colloidal Suspension	Coarse Suspension
Particle Size Range	<1 nm	1nm-100nm	100nm<

2.2.2 Nickel Speciation

Richens (1997) states that the hydrolysis of $[Ni(H_2O)_6]^{2+}$ is not extensive and requires alkaline solutions to generate $[Ni(H_2O)_5OH]^{+}$ prior to the precipitation of green hydrous $Ni(OH)_2$ at around pH 10. At high concentrations, above 0.1M, the tetranuclear species $Ni_4(OH)_4^{4+}$ is formed above pH 8 and at pH values above 12 the soluble tetrahedral anions $Ni(OH)_3(H_2O)^-$ and $Ni(OH)_4^{2-}$ are present. (Richens 1997, pp. 491-9).

The solubility values for these products as compiled by Richens (1997) are listed in Table 3. The hydrolysis behaviour of aqueous Co^{2+} parallels that of Ni^{2+}. (Richens 1997, pp. 491-9)

Table 3 - Nickel hydrolysis products and solubility values for Hydroxo Nickel species (Richens 1997, pp. 491-9)

Species	pKxy
$NiOH^+$	9.86
$Ni_4OH_4^{4+}$	27.7
$Ni(OH)_3^-$	30
$Ni(OH)_4^-$	>44

[3] See Definitions

The stability constant of each species within the nickel hydroxide and sulphate system, as compiled by Sist (2004), are given in Table 4.

Table 4 - Nickel hydroxide and sulphate stability constants at various ionic strengths at 25°C (Sist 2004, p. 157)

Complex	Stability Constant Log(B)				
Ionic Strength	I = 0	I = 0.1	I = 1	I = 2	I = 3
Ni^{2+} [4]	-17.2	-17.25	-16.99	-16.9	-16.85
$NiOH^{+}$	4.14	4.044	3.779	3.691	3.642
$Ni(OH)_2$ (aq)	9	8.804	8.539	8.451	8.402
$Ni(OH)_3^{-}$	12	11.79	11.79	11.79	11.79
$Ni(OH)_4^{2-}$	12	12.151	12.682	12.857	12.956
Ni2OH+++	3.3	3.546	3.811	3.899	3.948
Ni4(OH)4++++	28.26	28.491	29.022	29.197	29.296
NiSO4	2.32	-	0.57		0.26
Si(SO4)2--	1.02	-	1.42*[5]	-	-

The pH of formation of the nickel hydroxide precipitation specified by Richens (1997) is in direct contrast to the HSC and Factsage databases and subsequent Eh pH diagrams.

In contrast to this speciation work carried out by Sist (2004) and Richens (1997), Shankar & De Souza (1963) concluded that the simple metal hydroxide reaction given in Equation 14 was sufficient to explain the precipitation of nickel hydroxide because polymerisation and nickel ion speciation was not significant in concentrations less than 0.01 M. (Shankar & De Souza 1963)

Equation 14 - Typical metal hydroxide formation reaction

$$M^{2+} + 2OH^{-} \leftrightarrow M(OH)_2(s)$$

[4] Solubility product for $Ni(OH)_2$ dissolution

[5] Values uncertain

There is significant literature disagreements regarding the free energy of formation of the species involved in the formation of the metal hydroxide precipitates in question. Table 5 gives the free energies of nickel cobalt and hydroxide ions sourced from HSC (1986) and Factsage (2001).

Table 5 – Literature sourced free energies of formation of the reactant species

Species	Free Energy of Formation (kJ/mol)	Source
Ni2+	-46	Bard, Parsons and Jordan (1985).
	-45.6	HSC
	-15.552	Factsage
Co2+	-55.6	Bard, Parsons and Jordan (1985).
	-61.835	HSC
	-24.476	Factsage
OH-	-157	Bard, Parsons and Jordan (1985).
	-	HSC
	-226.744	Factsage

Figure 1 shows the Eh pH diagram for nickel developed in HSC. For the solution potentials relevant to this thesis, around 0 V, HSC calculates that nickel hydroxide should precipitate approximately above pH 5.2.

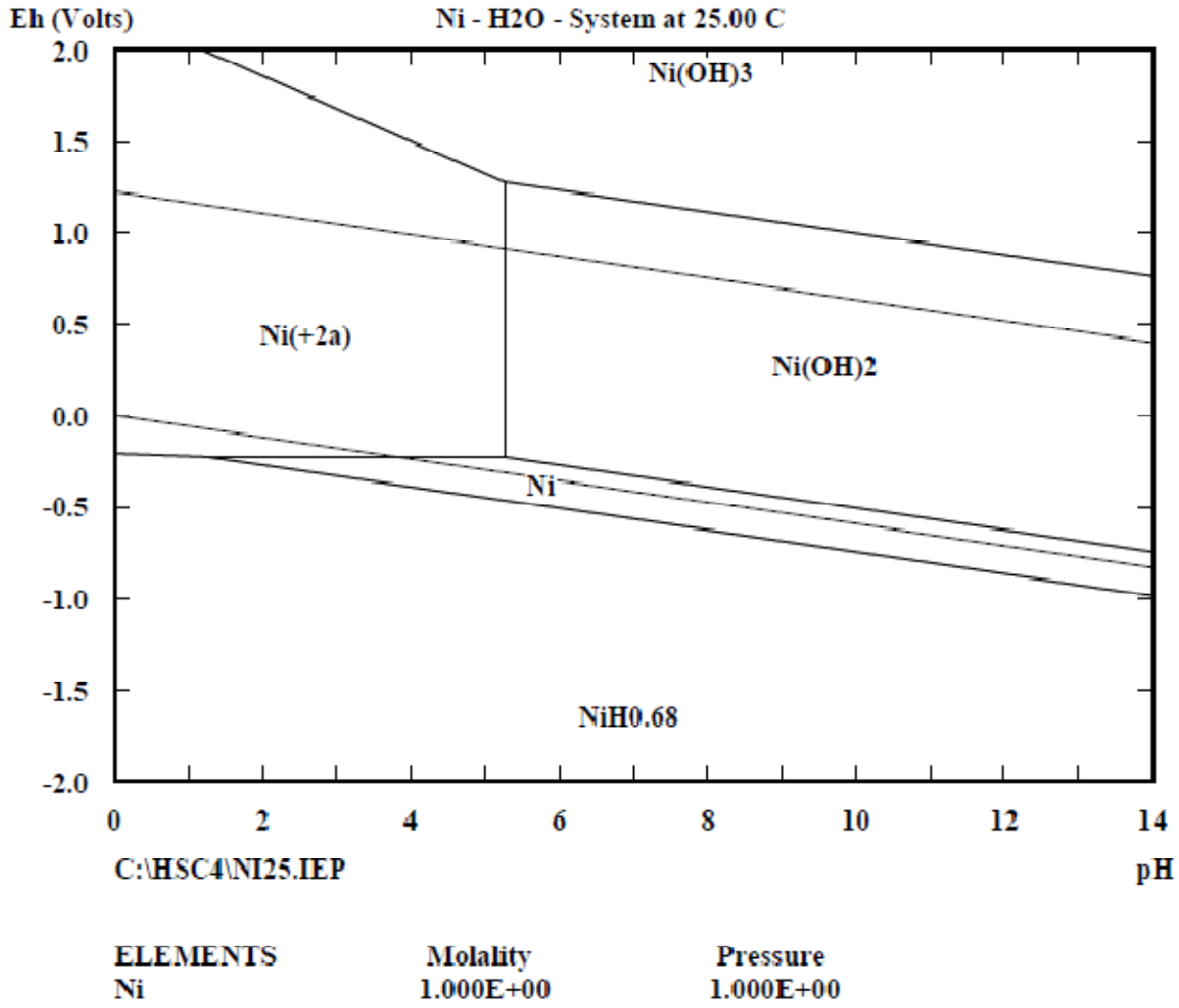


Figure 1 - Nickel Eh pH diagram developed in HSC* (*HSC* 1986)

* This Eh pH diagram was calculated ignoring NiO (s) which HSC calculates is predominant in the region where $Ni(OH)_2$ is known to dominate. It is assumed that there is an error in the calculations.

Figure 2 shows the Eh pH diagram for nickel developed in Factsage. For the solution potentials relevant to this thesis, around 0 V, Factsage calculates that nickel hydroxide should precipitate approximately above pH 6.25.

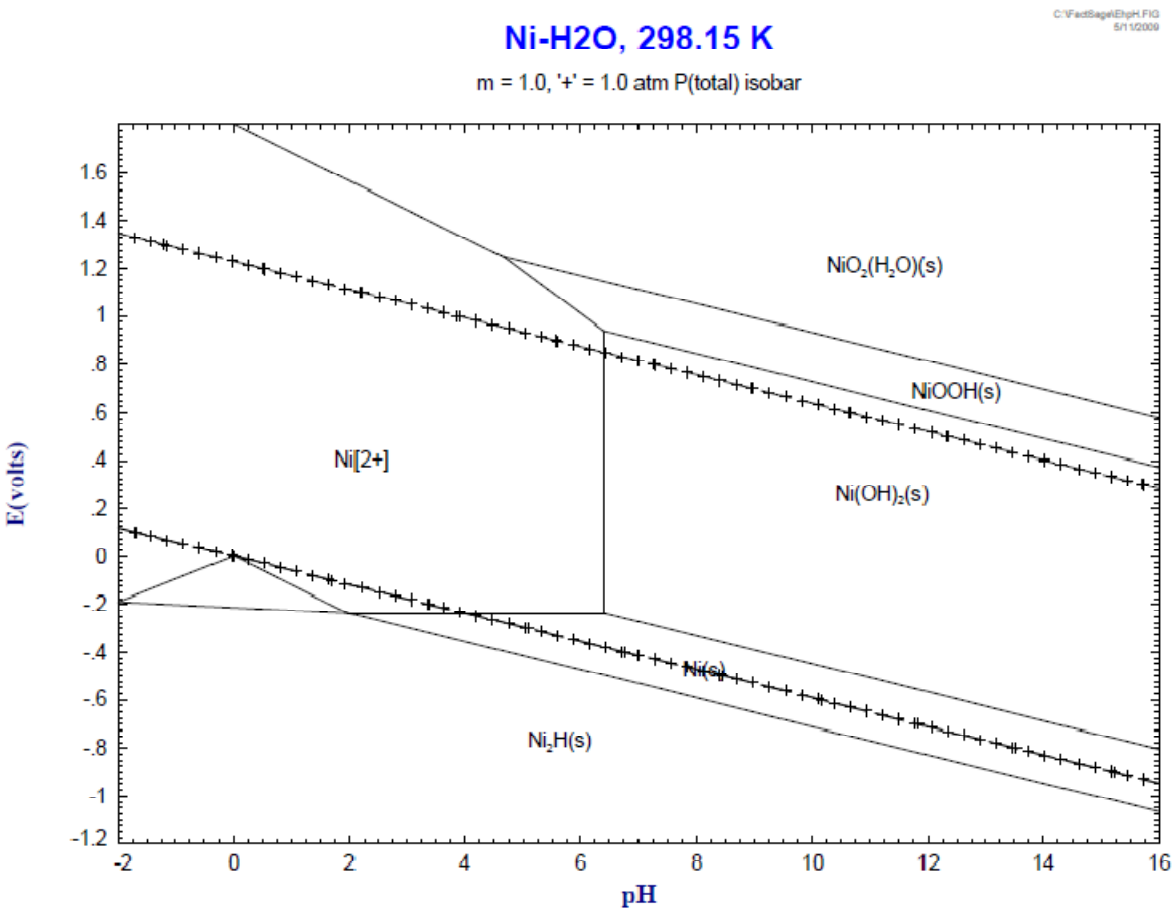


Figure 2 - Nickel Eh pH diagram developed in Factsage (*Factsage* 2001)

Figure 3 shows the Eh pH diagram for cobalt developed in HSC. For the solution potentials relevant to this thesis, around 0 V, HSC calculates that cobalt hydroxide should precipitate approximately above pH 6.0. The cobalt hydroxide should then become less stable and form solid cobalt oxide, Co_3O_4 above a pH of about 9.

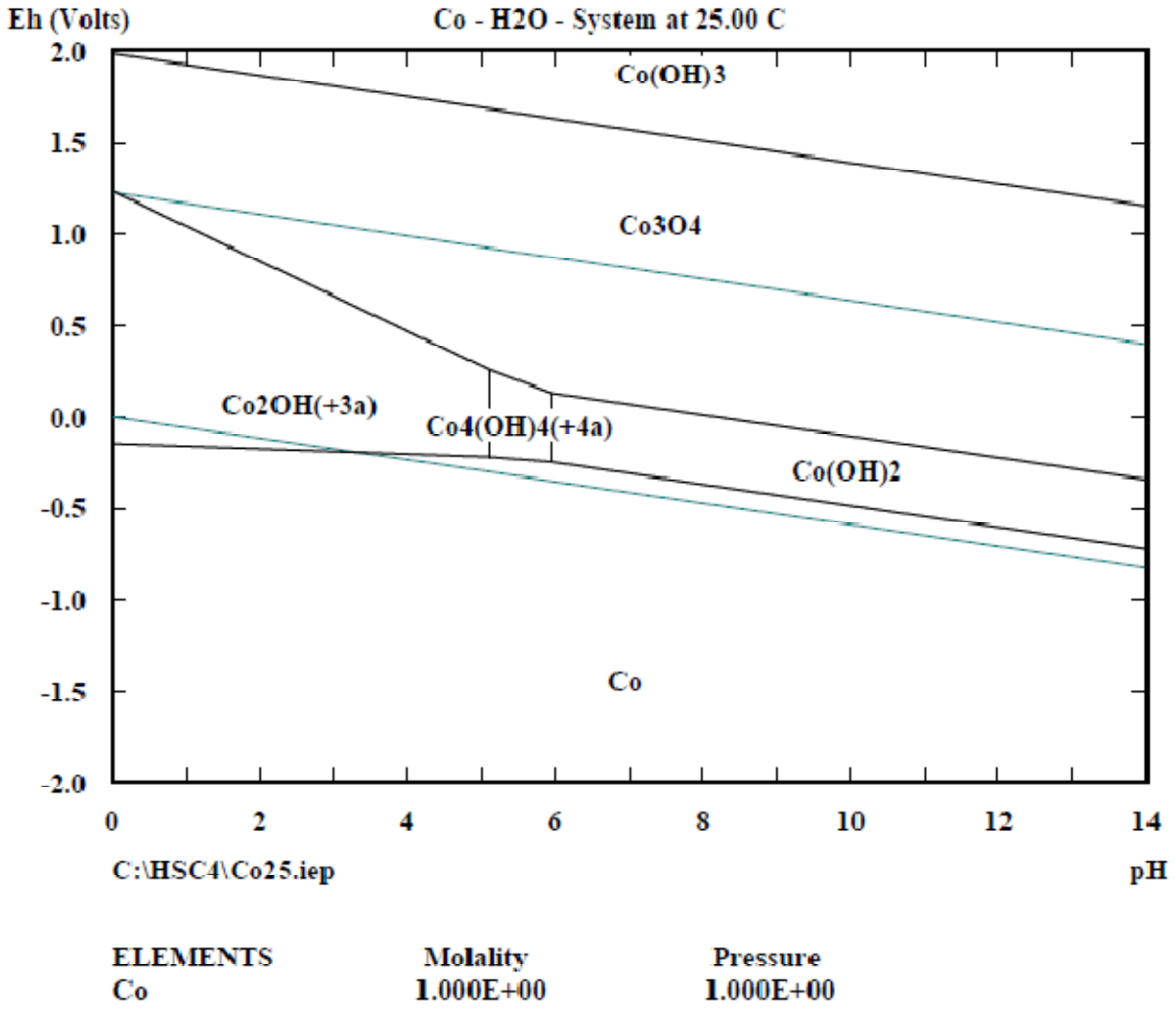


Figure 3 – Cobalt Eh pH diagram developed in HSC (*HSC* 1986)

Figure 4 shows the Eh pH diagram for manganese developed in HSC. For the solution potentials relevant to this thesis, around 0 V, HSC calculates that manganese hydroxide is only stable over a short pH range. The hydroxide should precipitate above pH 7.7 and then become less stable and form solid manganese oxide, Mn_3O_4 above a pH of about 8.2. Below pH 6 the cobalt is most stable as hydroxide complexes.

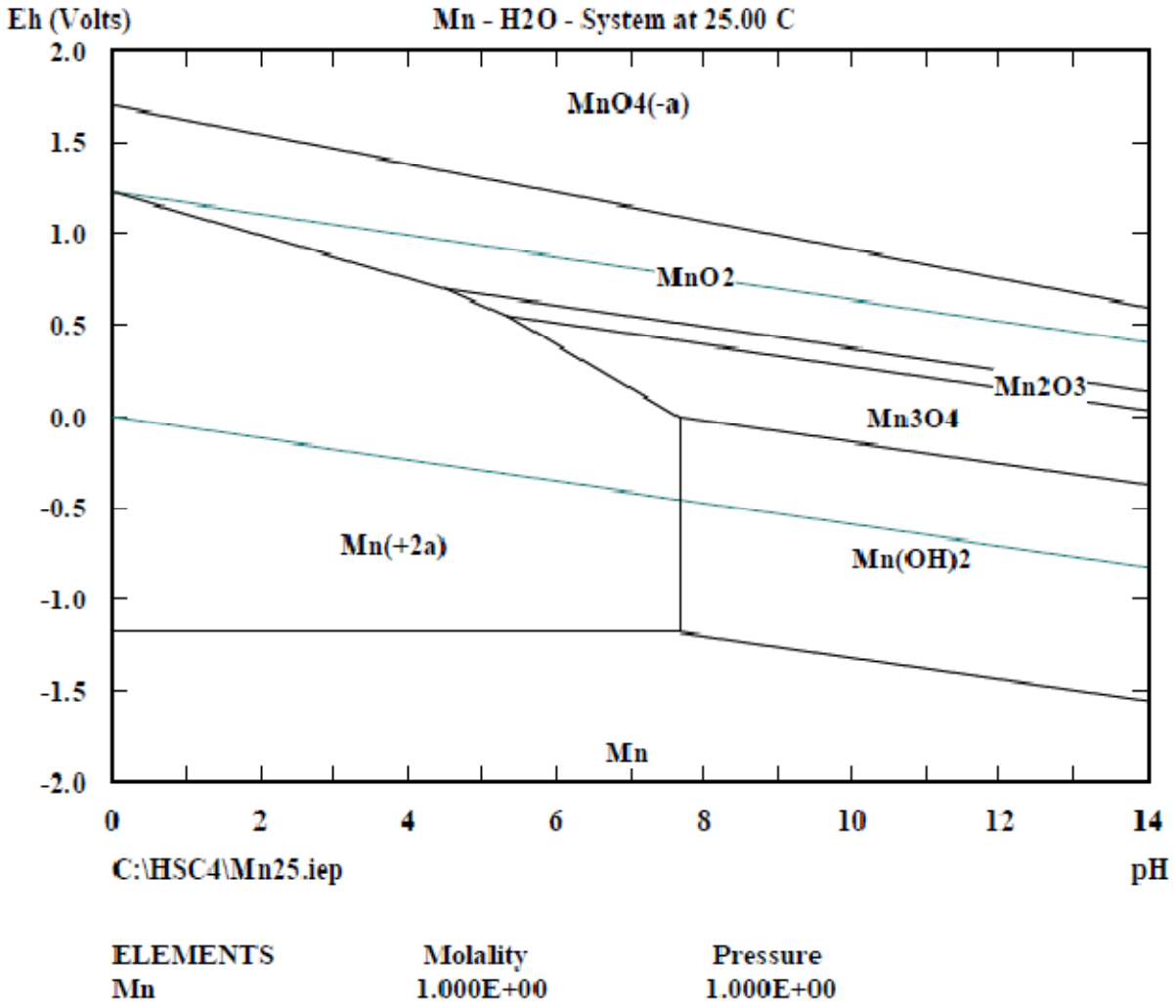


Figure 4 - Manganese Eh pH diagram developed in HSC (*HSC* 1986)

2.3 Industrial Nickel Processing

2.3.1 Minerals

The most important commercial deposits of nickel are garnierite deposits and nickel substituted pyrrhotite deposits. Interestingly, cobalt only occurs in nature in association with nickel. (Cotton & Wilkinson 1988, pp. 724-55).

Garnierite is not a single mineral but a mixture of magnesium-nickel hydro silicates such as serpentine, talc, sepiolite, chlorite and smectite. It forms by lateritic weathering of ultramafic rocks (Brindley & Hang 1973).

The mineral pyrrhotite has the chemical formula Fe(n)S(n+1) and can contain some nickel replacing the Fe(II). The extent of substitution is usually between 3 to 5% for the commercially recognised nickel resources (Cotton & Wilkinson 1988, pp. 724-55).

2.3.2 Laterite Deposits

Production of nickel from laterite ores has been carried out for over a century. Laterite processing began with the processing of garnierite from New Caledonia however until now the majority of the worlds nickel supply has been predominantly derived from sulphide sources. In the future, the production of nickel from sulphide ores is predicted to remain relatively constant with the majority of the expansion of nickel production capacity required to meet the growing demand coming from the processing of lateritic ores.(Dalvi, Bacon & Osborne 2004)

Laterisation is the process of weathering that can occur in certain rocks over long periods of time. The laterisation of ultramafic rocks gives rise to a strong dissolution and removal of magnesium and silicium which leads to a residual concentration of iron and nickel in a goethite-rich limonite surface layer. A portion of the nickel is also leached downwards and fixed in the underlying decomposed ultramafic rock. This process gives rise to both a moderate increase in nickel concentration in the decomposed ultramafic rock forming nickel silicates and nickel saprolite and also relatively small amounts of nickel-rich garnierite ore precipitated in any hollow spaces down through the rock (Brindley & Hang 1973).

Laterite ores typically contain nickel grades between about 1 – 3% with the nickel relatively evenly distributed throughout the ore body. They can also contain up to 0.25% cobalt which becomes a very important constituent to the profitability of the ore body profitability. (Krause, Singhal & Blakey 1997)

2.3.3 General Processing Methods

The metallurgy of nickel is complicated and varies significantly between the particular ore being processed. Nickel ores can be split into two major types – sulphides where the nickel is substituted into pyrrhotite, and laterites where the nickel is bonded to silicates along with many other metals. These two types of nickel ore require distinctly different processing methods.

Sulphides

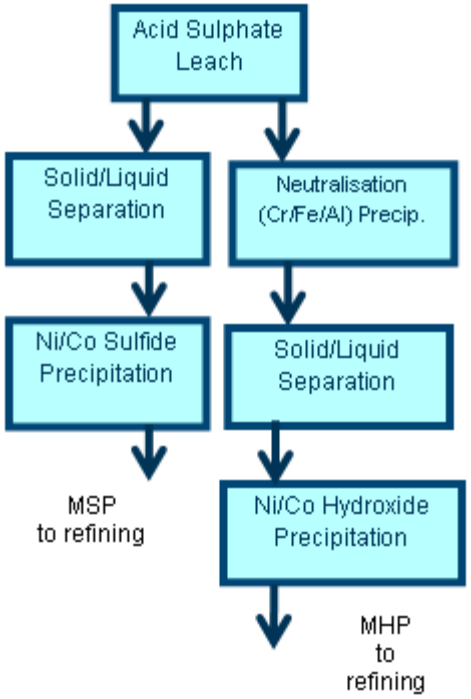
Sulphide ores are usually concentrated using flotation and then transformed into Ni_2S_3 which is roasted in air to form NiO. This is then reduced using carbon to form metal of moderate purity (Cotton & Wilkinson 1988, pp. 724-55).

High purity nickel can then be formed using the carbonyl process, where carbon monoxide is reacted with impure nickel at 50°C and atmospheric pressure or with a nickel-copper matte under strenuous conditions. This forms volatile $Ni(CO)_4$, which is then thermally decomposed at 200°C to obtain Nickel of 99.90 to 99.99% purity (Cotton & Wilkinson 1988, pp. 724-55).

Laterites

Laterite ores cannot be processed through the traditional method of smelting because they cannot be concentrated through flotation, as with sulphide ores. This means the volume of ore required for treatment is massive and the smelting energy requirements would be equally massive (Sist 2004, p. 31). Instead laterites are usually processed using a leach process often operated at high temperatures and pressures in order to adequately dissolve the nickel minerals. The leach process can be followed by a number of extraction or purification methods such as solvent extraction or precipitation. Figure 5 outlines two laterite processing methods employing the sulphuric acid leach followed by either mixed sulphide precipitation or mixed hydroxide precipitation.

Figure 5 – Sulphuric acid to precipitation nickel laterite processing routes (Vaughan 2009, p. 18)



As of 2004, the high pressure acid leach (HPAL) process was being commercially employed in four plants around the world to treat limonitic laterites and a number of new plants employing the process were being developed and built. Depending on the ore type, the HPAL can be operated under Platsol conditions to dissolve both base and precious metals within the autoclave simultaneously (Ferron & Fleming 2004). The Platsol process involves adding chloride ions, usually in the form of sodium chloride to the leach. This allows for high levels of base and precious metal extraction from the concentrate under total oxidation conditions at 225º C and about 100 psig of oxygen overpressure. The PGM and gold are extracted by forming complexes with chloride.(Dreisinger et al. 2005)

2.3.4 Ravensthorpe Nickel Operation

Ravensthorpe Nickel Operation in Ravensthorpe, Western Australia is nickel processing plant that will produce 50000 t/annum nickel and 1400 t/annum cobalt as mixed hydroxide precipitate (MHP) at full production (White, Miller & Napier 2006). As Ravensthorpe employs the MHP processing method to produce its nickel product, it will be used as an example of the commercial production of nickel hydroxide. The Ravensthorpe process is described at the block diagram level in Figure 6.

Figure 6 - Ravensthorpe Nickel Operation in Ravensthorpe, Western Australia (Harvey 2008, p. 16)

Beneficiation (BENE)

- Upgrade of the nickel/cobalt values in the ore by rejecting the low-grade, coarse size fractions
- Limonite and saprolite ores are upgraded separately from 1.03 and 0.79 % nickel to 2.17 and 1.40 % nickel, respectively (White, Miller & Napier 2006). Approximately 60 % of the ore is rejected.

Enhanced Pressure Acid Leaching (EPAL)

- Pressure acid leaching of beneficiated limonite slurry at 250 °C and 4500 kPag.
- Atmospheric leaching of beneficiated saprolite slurry at 95 °C
- Nickel/cobalt extractions exceed 96%. Extraction of major impurities iron, aluminium, manganese, magnesium and chromium exist.

Induced Jarosite Precipitation (IJP)

- Precipitation and neutralisation of excess ferric iron and acid, respectively
- Recycled SN solids help metal recovery, acid neutralization and precipitation kinetics

Primary Neutralisation (PN)

- Removal of ferric iron as jarosite and lesser aluminium and chromium
- pH 2.5 with effectively 98% precipitation of ferric demonstrated in pilot runs
- Total retention time up to 5 hours, benefiting from 90 °C liquors

Counter-Current Decantation (CCDs)

- Separation of the leach liquor from the barren solids and precipitates (to tailings)
- Wash ratios between 2.5 and 4.3 achieve greater than 98% Ni wash efficiencies with up to 54% solids in the underflow demonstrated in pilot runs (Adams et al. 2004)
- Six CCDs and process water from MnR is added to the last CCD as wash water

Secondary Neutralisation (SN)

- Last chance to remove the last of the iron and aluminium ahead of MHP
- Oxidation of ferrous iron to ferric and hydrolysis of aluminium facilitates removal
- Lime addition to pH 5 and 10 hour residence time required

Ni/Co Mixed Hydroxide Precipitation (MHP)

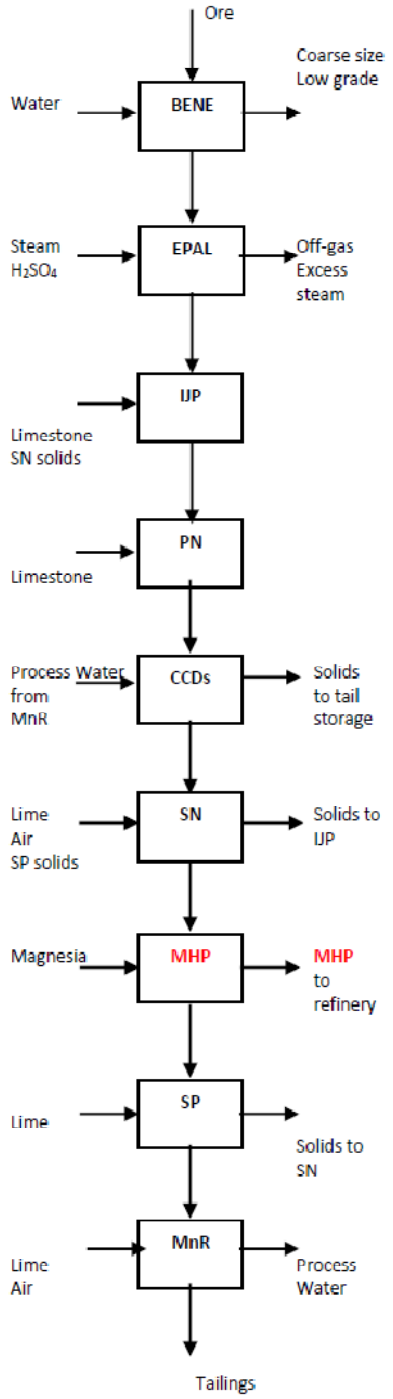
- Selective precipitation of Ni and Co (>90%) over Mn (~40%) using 0.82 t MgO/t Ni to pH 7.5 with a residence time of 3 hours using 3 main tanks
- MHP is thickened, washed-filtered and pressure filtered prior to despatch
- Seed is recycled (thickener underflow) to improve settling and filtration rates, increase MgO utilization and act as a substrate for new MHP to precipitate on

Scavenger Precipitation (SP)

- Recovery of remaining Ni and Co while leaving significant Mn and Mg in solution
- Thickened solids are recycled to SN to increase Ni/Co recoveries

Manganese Removal (MnR) and Tailings Storage

- Precipitation and thickening of the bulk of Mn left in solution for tailings storage
- Thickener overflow is recycled as process water to CCDs
- Tailings dam provides water balance control by evaporation and is the final repository of dissolved salts such as magnesium sulphate



As shown in Figure 6, the Ravensthorpe process precipitates nickel and cobalt as hydroxides from the sulphuric acid leach solution using magnesia. Any manganese dissolved in the leach

solution can also precipitate. Manganese is an impurity in the mixed hydroxide precipitate so the process is manipulated such that the extent of manganese precipitation is limited while still attempting to maintain high recovery of nickel and cobalt. The simplified overall precipitation reactions for nickel hydroxide, cobalt hydroxide and manganese hydroxide are given in Equation 15, Equation 16 and Equation 17 respectively.

Equation 15 - Nickel Hydroxide Precipitation

$$NiSO_{4(aq)} + MgO_{(s)} + H_2O_{(l)} \rightarrow Ni(OH)_{2(s)} + MgSO_{4(aq)}$$

Equation 16 - Cobalt Hydroxide Precipitation

$$CoSO_{4(aq)} + MgO_{(s)} + H_2O_{(l)} \rightarrow Co(OH)_{2(s)} + MgSO_{4(aq)}$$

Equation 17 - Manganese Hydroxide Precipitation

$$MnSO_{4(aq)} + MgO_{(s)} + H_2O_{(l)} \rightarrow Mn(OH)_{2(s)} + MgSO_{4(aq)}$$

The mixed hydroxide precipitate is then shipped to the Yabulu Refinery in Yabulu, Queensland, where it is re-leached, the metals are separated and refined to produce products for sale. (Harvey 2008, pp. 17-8)

2.3.5 **MHP**

SEM images of Ravensthorpe mixed hydroxide precipitate carried out by White, Miller & Napier, 2006, show the precipitate forming fine, micron scale particles. The particles appear to be amorphous as no regular and repeating crystal structure is apparent. Agglomeration is evident as the particles exhibit irregular lumps. The particle surface morphology shows short dendrite formation – the length of the dendrites may be minimized by attrition between the particles. (Harvey 2008, p. 32)

The moisture content of the MHP is strongly dependent on the form of the precipitate and the filtration equipment used. Poorly formed, amorphous precipitates hold significantly more moisture than well-formed crystalline precipitates and are much harder to filter effectively. A belt filter wash stage is used at Ravensthorpe and product moisture is typically 40%. The MHP is then pressure filtered for dispatch to Yabulu. (Harvey 2008, p. 32)

The precipitate form depends very much on the precipitating conditions. When an amorphous, gelatinous precipitate is formed, the average particle size is very fine while a well-formed precipitate exhibiting some crystallinity will have much larger, visible particles. Larger particle sizes are desired due to the ease of filtering and handling but extending the number of seed

recycle stages can result in generation of finer particles due to coarse particle attrition (Sist & Demopoulos 2003). There is obviously an optimal seeding ratio that needs to be determined in order to produce predominantly coarser particles. (Harvey 2008, p. 30)

Other conditions can also affect the precipitate particle size, such as the temperature at which the precipitation is carried out at, the pH and concentration of each species within the system.

3. Derivation of Hypotheses

The literature review and scoping experimentation clearly show that investigations regarding nickel hydroxide gel-like precipitation should focus on two key areas when attempting to characterise the nickel hydroxide. The first area of investigation is regarding the properties of the gel-like precipitate in solution during and after the precipitation reaction. The second area of investigation is regarding the nickel hydroxide precipitate once it has been decanted and filtered.
The precipitate properties of interest are:

- Solubility and free energy of formation of the precipitate compared to literature values
- Hydration and atomic structure of the precipitate
- Speciation within the system
- Precipitate particle size and settling rate
- Temperature and contaminant effects on the above

The filtered precipitate properties of interest are:

- Phase and physical properties
- Hydration and atomic structure of the filtered precipitate
- Temperature and contaminant effects on the above

Hypotheses, regarding both the precipitate in solution and after filtering, have been developed. Each hypothesis targets a specific factor of the characterisation and processing of nickel hydroxide outlined by the thesis aims.
The major hypotheses addressing the characterisation of the nickel hydroxide gel-like precipitate are:

1. Nickel Hydroxide is a separate phase from crystalline nickel hydroxide, with its own free energy of formation

This hypothesis is aimed at differentiating the nickel hydroxide precipitated at room temperature from crystalline nickel hydroxide.

2. The nickel hydroxide precipitation formed at room temperature is an enantiotropic (reversible metastable) phase that only occurs under certain temperature conditions

Assuming that hypothesis 1 is true, this hypothesis is aimed at understanding the temperature conditions under which the non crystalline nickel hydroxide is formed

3. Nickel hydroxide gel-like precipitate is hydrated and will decompose to a crystalline phase over time

This hypothesis is aimed at understanding the chemical structure of the precipitate and investigating the reaction equilibrium. It will show whether the nickel hydroxide precipitate is truly at equilibrium, verifying the results from hypothesis 1 and 2.

4. The nickel hydroxide gel-like precipitate forms individual colloidal particles from 1-100 nanometres

This hypothesis is aimed at understanding the physical properties of the precipitate. The results will provide further observational results to verify the phase for hypothesis 1.

A number of other hypotheses have been developed to investigate specific areas of interest to the nickel hydroxide precipitation relating to industrial practices:

5. Cobalt hydroxide precipitation carried out at room temperature is very similar to nickel hydroxide precipitation carried out at room temperature

This hypothesis is aimed at finding whether cobalt hydroxide displays the same precipitation properties as nickel hydroxide does when formed at room temperature.

6. Nickel hydroxide stabilises cobalt in the solid phase

This hypothesis is aimed at understanding the interactions between nickel and cobalt relating to industrial mixed hydroxide precipitation.

7. Cobalt is stabilised in the solid phase by manganese

This hypothesis is aimed at understanding the interactions between cobalt and manganese relating to industrial mixed hydroxide precipitation. Manganese and cobalt are known to have an affiliation with each other in geochemistry.

8. The other typical MHP system constituents have a significant effect on the precipitate properties

This hypothesis aims to understand some of the interactions involved in the formation of mixed hydroxide precipitate.

4. Experimental Design

In order to address the hypotheses, an experimental plan was required. Firstly, a method of validating each hypothesis was established.

Hypothesis 1: Nickel Hydroxide precipitated at room temperature is a separate phase from crystalline nickel hydroxide, with its own free energy of formation

The free energy of formation of the precipitate can be approximated using the reaction of formation equilibrium constant. The equilibrium constant can be calculated using the concentration of the chemical species involved in the reaction. This relies on the reaction having achieved equilibrium at the time of testing.

The phase of the precipitate is much harder to categorise and prove. Within solution, observation and particle sizing are the only experimental methods available for analysis. The filtered precipitate phase can be indicated by observation and SEM, FTIR and XRD methods.

Hypothesis 2: The nickel hydroxide precipitation formed at room temperature is an enantiotropic (reversible metastable) phase that only occurs under certain temperature conditions

The free energy of formation identified by hypothesis 1 will give indication on the metastability of the precipitate. If the free energy of formation of the precipitate is higher than the literature values for the crystalline nickel hydroxide phase this indicates that the precipitate is metastable. Calculating the free energy of formation for the precipitation reaction when reacted at a higher temperature will demonstrate if the same metastable product as at room temperature is formed.

The reversibility of the precipitation reaction at room temperature can be tested by precipitating then redissolving the precipitate observing any differences in precipitation and redissolution pH.

Hypothesis 3: Nickel Hydroxide precipitated at room temperature is hydrated and will decompose into the crystalline phase over time

The hydration of both the filtered and in solution precipitate can be approximated using the mass difference between the pure nickel hydroxide precipitated and the filter cake or decanted precipitate. Assuming the excess mass is due to water molecules, the hydration factor can be calculated.

There are a number of ways of verifying if the precipitate decomposes into the crystalline phase over time. For the precipitate in solution, measuring the pH and recalculating the free energy of

formation based on any changes in equilibrium over time will give indication on whether the precipitate is decomposing. For the filtered precipitate, observing any changes and recalculating the hydration factor will give indication on whether the precipitate is decomposing.

Hypothesis 4: Nickel hydroxide precipitated at room temperature forms individual colloidal particles from 1-100 nanometres

The University of Queensland has a Malvern Mastersizer 2000 which is reported to size particles down to sub-micron scale although issues are for seen with clogging the instrument. There are no methods of sizing colloidal precipitate particles when in solution available at the University of Queensland. Scientex from Victoria, AUS and Matec Applied Science from Massachusetts, USA have offered to test some samples using their acoustic particle sizing equipment which is accurate down to 10 nanometres. The filtered precipitate particle size can be analysed down to the micron scale using SEM.

Hypothesis 5: Cobalt hydroxide precipitation carried out at room temperature is very similar to nickel hydroxide precipitation carried out at room temperature

The similarities and differences between cobalt and nickel hydroxide precipitation can be observed by applying the first 4 hypotheses to cobalt hydroxide precipitation. Completely repeating all of the experiments replacing nickel with cobalt is outside the scope of this thesis but select experiments could give indication as to the similarities and differences.

Hypothesis 6: Nickel hydroxide stabilises cobalt in the solid phase

The interactive effects of mixed nickel and cobalt can be observed by applying the first 4 hypotheses to a mixed nickel and cobalt system and comparing with the individual standard systems. Completely repeating all of the experiments with individual and mixed nickel and cobalt system is outside the scope of this thesis but select experiments could give indication as to the interactions.

Hypothesis 7: Cobalt is stabilised in the solid phase by manganese

The interactive effects of mixed cobalt and manganese systems can be observed by applying the first 4 hypotheses to a mixed cobalt and manganese system and comparing with the individual standard systems. Completely repeating all of the experiments with individual and mixed cobalt

and manganese system is outside the scope of this thesis but select experiments could give indication as to the interactions.

Hypothesis 8: The other typical MHP system constituents have a significant effect on the precipitate properties

The interactive effects of typical industrial system constituents can be observed by applying the first 4 hypotheses to simplified industrial systems and comparing with the individual standard systems. Completely repeating all of the experiments with a simplified industrial system is outside the scope of this thesis but select experiments could give indication as to the interactions.

Two types of experiments were developed which, by design, could achieve all of the required experimental results

Complete titration experiments

When the amount of hydroxide added to a nickel system is greater than 100% of the amount required to precipitate all of the nickel, all of the nickel will precipitate. As the original nickel concentration is known, the mass of nickel hydroxide precipitate can be calculated. The complete titration curve can give information regarding the pH of precipitation and the hydroxide uptake. pH measurements taken over long time periods can give information about any precipitate/solution interaction. Filtering the samples provides a known mass of nickel hydroxide for further experimentation.

In order to test the reversibility of the precipitation reaction, the complete titration experiment was carried out and then reversed by adding acid instead of hydroxide.

Incomplete titration experiments

When the amount of hydroxide added to a nickel system is less than 100% of amount required to precipitate all of the nickel, the system should reach equilibrium between the hydroxide ion concentration, the nickel ion concentration, the reaction forming nickel hydroxide and the solubility of the nickel hydroxide. pH and concentration measurements taken over longer time periods can give information on the system equilibrium

5. Methods, Chemicals and Set-up

This section describes the experimental tools and conditions with which each experiment was carried out.

5.1 Titration Methods

5.1.1 Complete Titrations

The systems outlined in Table 6 were titrated until approximately 150% of the hydroxide required to form the complete metal hydroxide was added. The hydroxide was added in the form of sodium hydroxide and the calculations were carried out assuming that all the sodium hydroxide dissociated. The titrations were broken up into 10 15% additions. Scoping experiment results, described in the results section, showed that when the hydroxide additions were carried out every 2 minutes, the system did not reach equilibrium when compared with additions carried out every 30 minutes. For the remaining titration experiments, an addition rate of 30 minutes per titration was adopted to allow the system more time to achieve equilibrium. The scoping experiment did not prove that the system had come to equilibrium after 30 minutes but time constrains meant that a slower addition rate was not feasible.

Table 6 – Complete Titration Experiment Systems

System	Experimental Conditions
Nickel	100 mL@ 22 °C, 10*5mL additions of 20 g/L NaOH
Nickel 50dC	100 mL @ 50 °C, 10*5mL additions of 20 g/L NaOH
Nickel 80dC	100 mL @ 80 °C, 10*5mL additions of 20 g/L NaOH
Cobalt	100 mL @ 22 °C, 10*5mL additions of 2 g/L NaOH
Manganese	100 mL @ 22 °C, 10*5mL additions of 8.58 g/L NaOH
Nickel and cobalt	100 mL @ 22 °C, 10*5mL additions of 22 g/L NaOH
Nickel and magnesium	100 mL @ 22 °C, 10*5mL additions of 20 g/L NaOH
Nickel, cobalt, manganese and magnesium	100 mL @ 22 °C, 10*5mL additions of 30.58 g/L NaOH

In order to test the reversibility of the precipitation reaction, the complete titration experiment was carried out and then reversed by adding acid at the same stoichiometric rate in the place of hydroxide.

5.1.2 Various Extent Titrations

The systems outlined in Table 7 were titrated using a method termed various extent titrations. Seven identical systems were set up for each experiment. The first system was titrated to 15% of the required hydroxide and each subsequent system was titrated a further 15% until the 7th system had received 105% of the required hydroxide.

Table 7 – Various Extent Experiment Systems

System	Experimental Conditions
Nickel	7* 100 mL @ 22 °C, up to 7*5mL additions of 20 g/L NaOH
Nickel 50dC	7*100 mL @ 50 °C, up to 7*5mL additions of 20 g/L NaOH
Cobalt	7*100 mL @ 22 °C, up to 7*5mL additions of 2 g/L NaOH
Manganese	7*100 mL @ 22 °C, up to 7*5mL additions of 8.58 g/L NaOH
Nickel and cobalt	7*100 mL @ 22 °C, up to 7*5mL additions of 22 g/L NaOH
Cobalt and manganese	7*100 mL @ 22 °C, up to 7*5mL additions of 10.58 g/L NaOH

5.2 Chemicals and Set-up

5.2.1 Titrations

This thesis aims to investigate industrially applicable systems and as such, the typical industry metal species concentrations outlined in Table 8 were used. All experiments were carried with AR grade metal salts dissolved in distilled water. Bulk solutions were prepared and stored in volumetric flasks before being titrated. The titrations were carried out with 100 mL of solution in a baffled flask and constantly stirred by a magnetic bar & plate at sufficient speed to facilitate rapid mixing and attainment of steady pH values while not allowing air bubbles to be sucked into solution by the vortex. The pH values were considered stable when the measured value remained stable for 15 seconds. The pH determinations were made with TPS Model WP-80D

pH/Potential/Temperature Meter using a Model IJ44 – Temperature Compensated pH probe. This probe was standardised using 4.00 and 6.88 pH buffers. Experiments carried out at 50dC were controlled using the Thermoline Scientific Orbital Shaker Incubator and as such were shaken, not stirred, by the incubator. The experiments carried out at 80 °C were heated by

The titrations were carried out with NaOH solutions of sufficient concentration such that each addition required 5 mL of solution. These 5 mL additions were carried out using a Brand Tramserpipette automatic pipette.

Table 8 –Element concentrations used in the experiments

	Concentration g/L	Concentration M/L	Source
Nickel as nickel sulphate	5	0.009	NiSO4.6H2O
Cobalt as cobalt sulphate	0.5	0.008	CoSO4.7H2O
Manganese as manganese sulphate	2	0.036	MnSO4.H2O
Magnesium as magnesium sulphate	10	0.411	MgSO4.7H2O

5.2.2 Sampling and Storage

All titrated samples except those used to determine the settling rate were stored in 200 mL plastic lidded containers. The lids remained on each solution whenever possible to minimise any external effects such as evaporation or atmospheric oxidation, that is the lids were only taken off when pH measurements or samples were required. All titrated samples were pH tested at least one day, one week and one month after the titration. As these long term samples were not stirred, pH values took some time to steady. The pH was considered stable when the measured value remained constant for 30 seconds. The various extent titrations were sampled hourly, daily, weekly and monthly. 5 mL samples of the liquid phase were taken with the automatic pipette using a regularly cleaned pipette tip and stored in 10 & 15 mL covered test tubes. Because only the liquid phase was taking, aging of the sample was not an issue. Some of the samples taken on the day that the titration was carried out were not reliable as the slow settling rate meant that when attempting to sample the liquid phase, some of the solid phase was also removed.

5.2.3 UV Vis

The test tube samples were analysed using the Carly 50 UV Vis spectrometer for the sample absorbance in acrylic sample container with a 1 cm path length. This container allows a wavelength range of 285-750. 3.5 mL of each sample was transferred into the container and analysed then transferred back into the test tube. The container was then double washed with distilled water. The lowest concentration samples were tested first.

5.2.4 Atomic Absorption Spectroscopy

After Uv Vis analysis, the 5 mL samples were then standardised by adding 5 mL of 4% nitric acid before being diluted with 2% nitric acid to the required concentration in order to allow Atomic Absorption Spectroscopy. The AAS was carried out with the Perkin Elmer AAnalyst 400 and S10 Autosampler. The Perkin Elmer AAnalyst 400 manual was followed in selecting the appropriate wave length and standard concentration calibrations in order to obtain accurate results. The AAS standard solutions were prepared using Ultra Elemental Standards reagents.

5.2.5 Filtered Samples

Samples were filtered with 0.2 micron filter paper using a Capex 8C Vacuum Pump and washed with 100 mL of distilled water.

All equipment was cleaned with distilled water prior to use.

6. Results & Discussion

This section is structured around the two types of experiments carried out. The results are collated and discussed regarding the thesis aims of investigating the gel-like precipitates and the factors affecting their formation, defining the physical, chemical and thermodynamic properties of the nickel hydroxide gel-like precipitate and provide scoping work for further research.

6.1 Complete Titration Experiments

6.1.1 pH Results

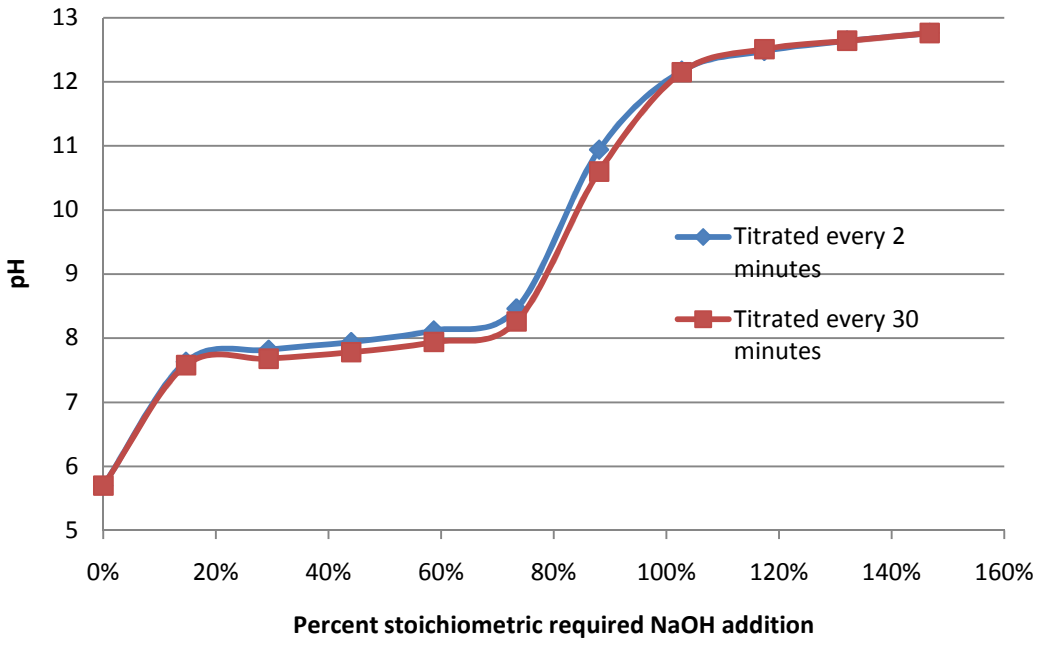


Figure 7 – Nickel hydroxide precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, undertaken at room temperature (~22 °C), NaOH addition vs pH, titrated every 2 minutes vs titrated every 30 minutes

Figure 7 shows that when the titration is carried out every 2 minutes, the system shows higher pH values than when the titration was carried out every 30 minutes through the precipitation stage. This indicates that system had not reached equilibrium through hydroxide consumption. Upon the addition of hydroxide, the area local to the hydroxide addition instantly formed precipitate. This shows that the area was above the critical supersaturation for the spontaneous precipitation of nickel hydroxide.

Figure 8 - Nickel hydroxide precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, undertaken at room temperature (~22 °C), titrated every 2 minutes

Figure 8shows the nickel hydroxide precipitate approximately 5 hours after being titrated. The precipitate clearly appears like a large green gelatinous mass with no clear structure or individual particles. There is a distinct phase boundary between the precipitate and the remaining liquid and the precipitate all settles as one. These factors all point to the precipitate being a gel as defined by Stokes and Frith (2008). They state that a gel is generally considered to have a low volume fraction of structuring agent or dispersed phase, such that there is an interconnected network structure whereby it is considered to be a percolated solid. This is clearly apparent as, assuming precipitant is complete $Ni(OH)_2$, the mass of the precipitant is only 0.79 grams dispersed in the 75 mL of gel phase. The settled as one mass to a point indicating that there is a significant network of attractive and repulsive forces holding the precipitate together while not allowing it to completely merge.

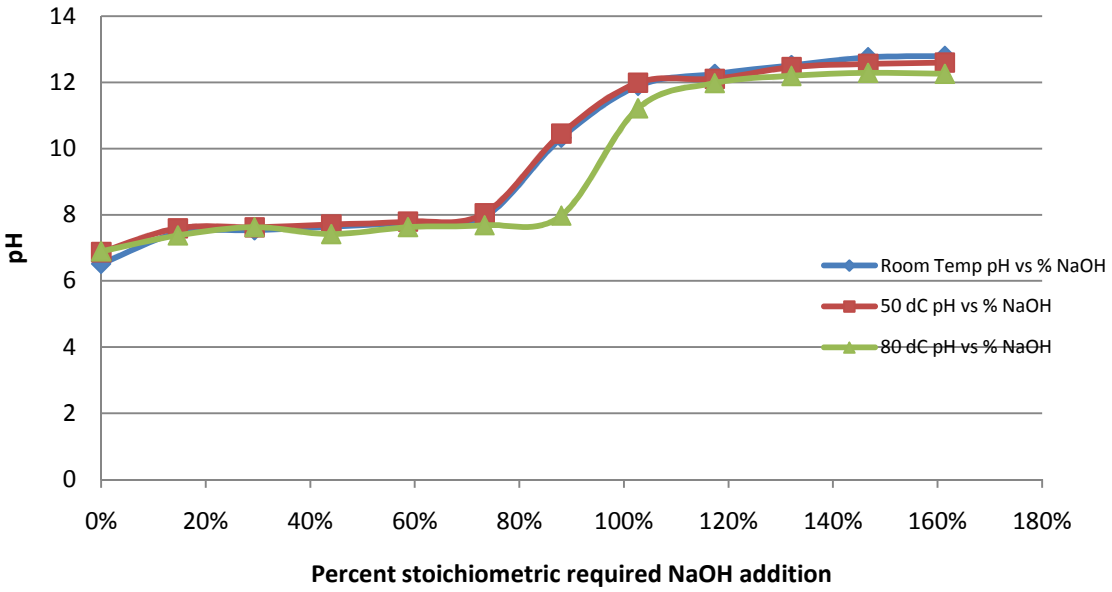


Figure 9 – Nickel hydroxide precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes, undertaken at room temperature (~22 °C), 50 °C & 80 °C, NaOH addition vs pH

In Figure 9 the precipitation stage for both the room temperature and 50dC was complete when only 75-90% of the required hydroxide was added while for the 80 °C system, the precipitation was complete when 90-105% of the hydroxide was added. In all cases the nickel precipitated between pH 7.8 to 8.1. This indicates that the nickel hydroxide precipitated at 80 °C is distinctly different from that precipitated at lower temperatures.

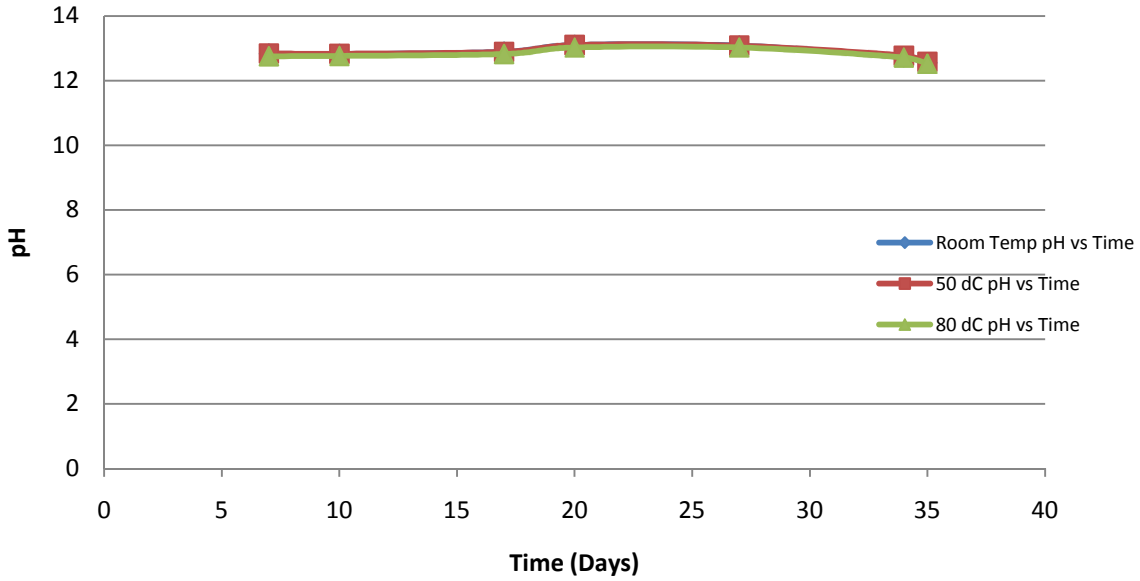


Figure 10 - Nickel hydroxide precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), 50 °C & 80 °C, pH change over time

Figure 10 shows that the nickel hydroxide precipitation experiments did no undergo any distinct pH shift over time. Once 150% of the required hydroxide was added to these systems they would be so far past the precipitation stage that any hydroxide intake by the solid would be insignificant.

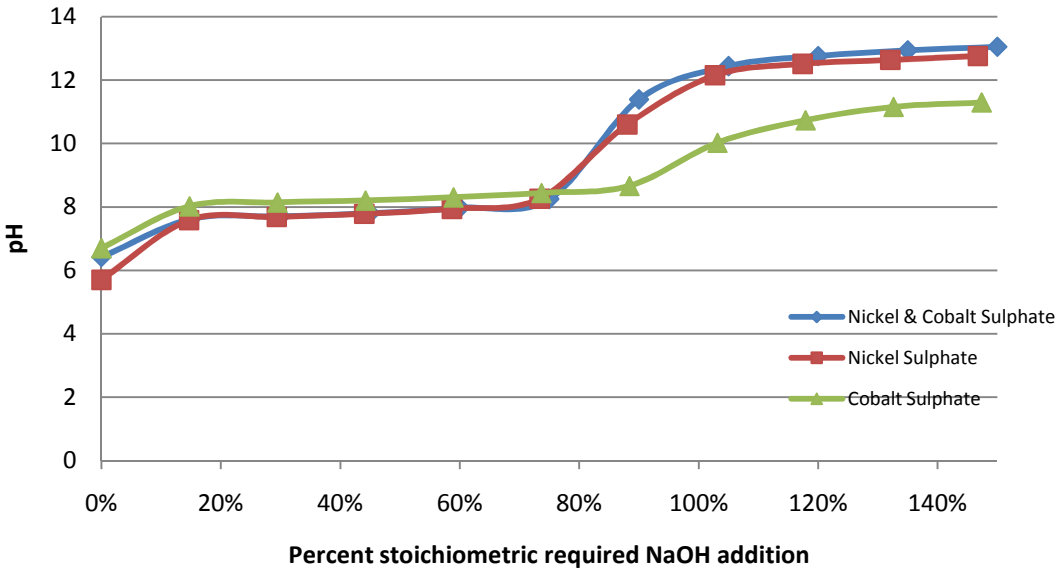


Figure 11 – Mixed nickel and cobalt precipitated from 100 mL of 5 g/L nickel, 0.5g/L cobalt in sulphate system with 5 mL additions of 22 g/L NaOH, nickel precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH & cobalt precipitated from 100 mL of 0.5 g/L cobalt in sulphate system with 5 mL additions of 2 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), NaOH addition vs pH

Figure 11 shows that cobalt precipitates between pH 8.0 to 8.2 and consumes 90-105% of the required hydroxide. The mixed nickel and cobalt system, with 5 g/L nickel and 0.5 g/L cobalt, only consumes 75-90% of the required hydroxide and precipitates between pH 7.8 to 8.0. There is no bump at pH 8.0 indicating the cobalt precipitating separately. Figure 12 actually shows how the cobalt (blue) appeared to be precipitating as soon as the hydroxide was added rather than the nickel (green). This is interesting as the cobalt concentration is approximately 10 times less than that of the nickel so the cobalt hydroxide solubility must be at least 10 times less than the nickel hydroxide and/or cobalt precipitates at much lower supersaturation levels.

Figure 12 – Image of Mixed nickel (green) and cobalt (blue) hydroxide being precipitated from 100 mL of 5 g/L nickel, 0.5g/L cobalt in sulphate system with 5 mL additions of 22 g/L NaOH

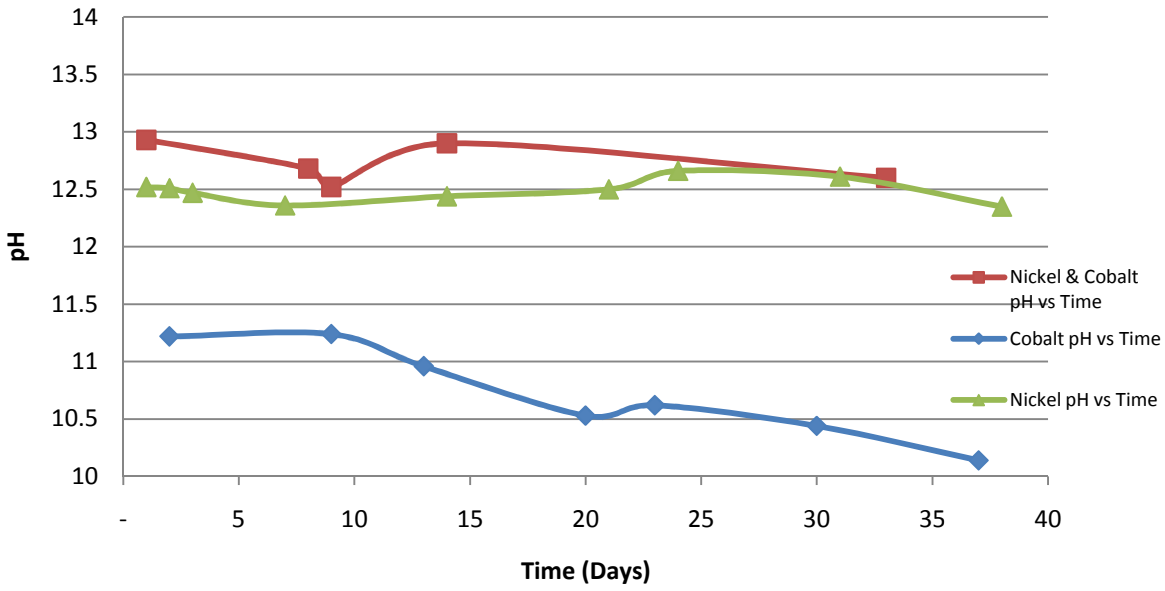


Figure 13 - Mixed nickel and cobalt precipitated from 100 mL of 5 g/L nickel, 0.5g/L cobalt in sulphate system with 5 mL additions of 22 g/L NaOH, nickel precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH & cobalt precipitated from 100 mL of 0.5 g/L cobalt in sulphate system with 5 mL additions of 2 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), pH change over time

Figure 13 shows both the nickel and mixed nickel and cobalt systems did not undergo any distinct pH shift over time while the cobalt system showed a clear drop in hydroxide concentration over time. The cobalt hydroxide precipitate was also observed to change colour over the month. Figure 14, Figure 15 and Figure 16 show the cobalt hydroxide colour at different stages of the aging process.

Figure 14 – Image of the cobalt hydroxide, freshly precipitated from 100 mL of 0.5 g/L cobalt in sulphate system with 5 mL additions of 2 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

Figure 14 shows freshly precipitated cobalt hydroxide. Individual clumps of precipitate can clearly be seen although they don't appear to be completely solid particles. It appears more like the gelatinous phase is dispersed in clumps throughout the liquid phase. Over time the clumps were observed to attract each other and settle into the one large mass of gel-like precipitate.

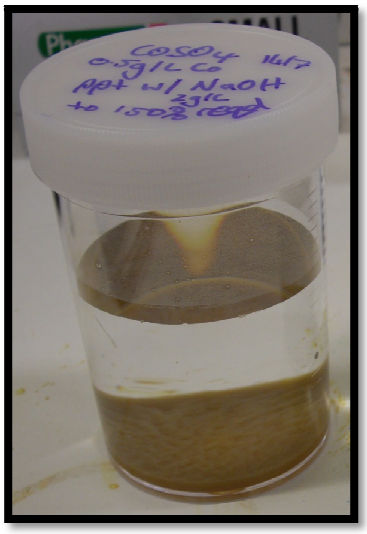


Figure 15– Image of the precipitated cobalt aged 1 day, precipitated from 100 mL of 0.5 g/L cobalt in sulphate system with 5 mL additions of 2 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

One day later the cobalt hydroxide precipitate had settled and changed colour. As per the Eh pH diagram shown in the literature review, the most stable phase at the pH that this sample was recorded at was Co_3O_4.

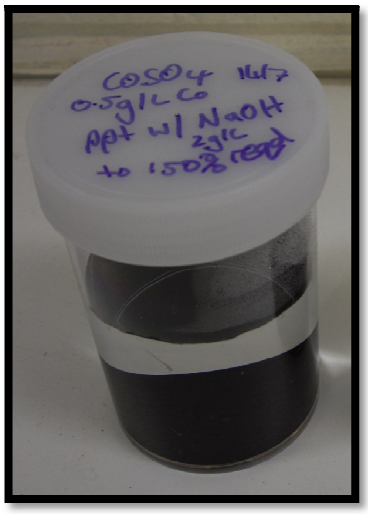


Figure 16– Image of precipitated cobalt aged 21 days, precipitated from 100 mL of 0.5 g/L cobalt in sulphate system with 5 mL additions of 2 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

The sample eventually ended up as shown in Figure 16.

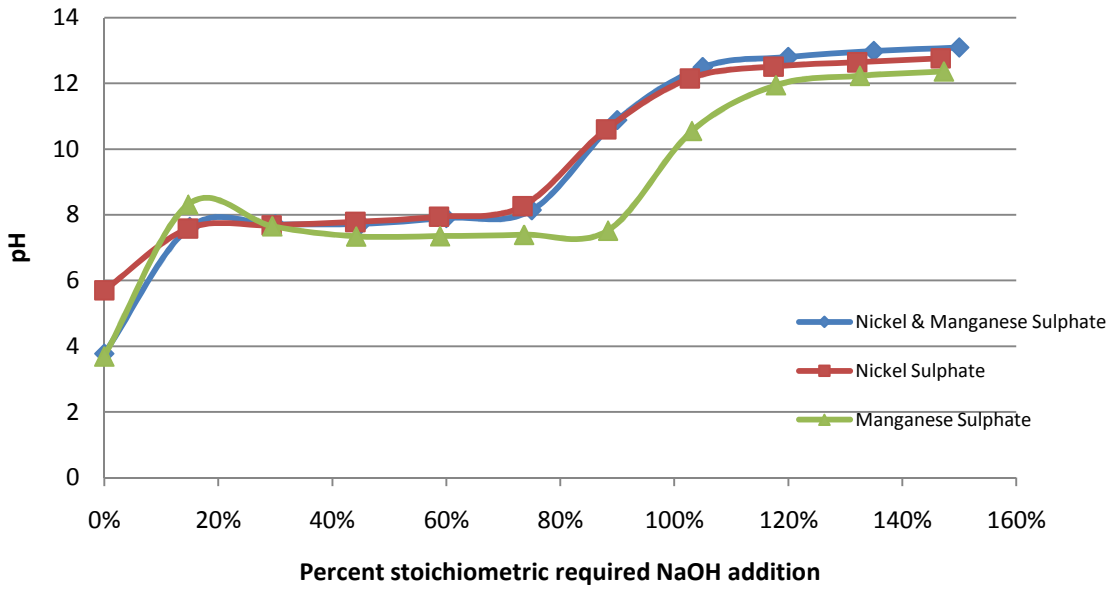


Figure 17 - Mixed nickel and manganese precipitated from 100 mL of 5 g/L nickel, 2g/L manganese in sulphate system with 5 mL additions of 28.58 g/L NaOH, nickel precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH & manganese precipitated from 100 mL of 2 g/L manganese in sulphate system with 5 mL additions of 8.58 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), NaOH addition vs pH

In Figure 17 manganese precipitation completes once 90-105% of the required hydroxide is added. After the first hydroxide addition the manganese did not take in much of the hydroxide as the pH increased to over 8.0, even though precipitation was observed. As more hydroxide was added the pH was observed to drop as low as pH 7.3 while the precipitation continued. When nickel and manganese at 5g/L nickel and 2 g/L manganese were precipitated together, the titration curve followed that of nickel with the precipitation stage between pH 7.8 and 8.1 and completing when 75-90% of the required hydroxide was added.

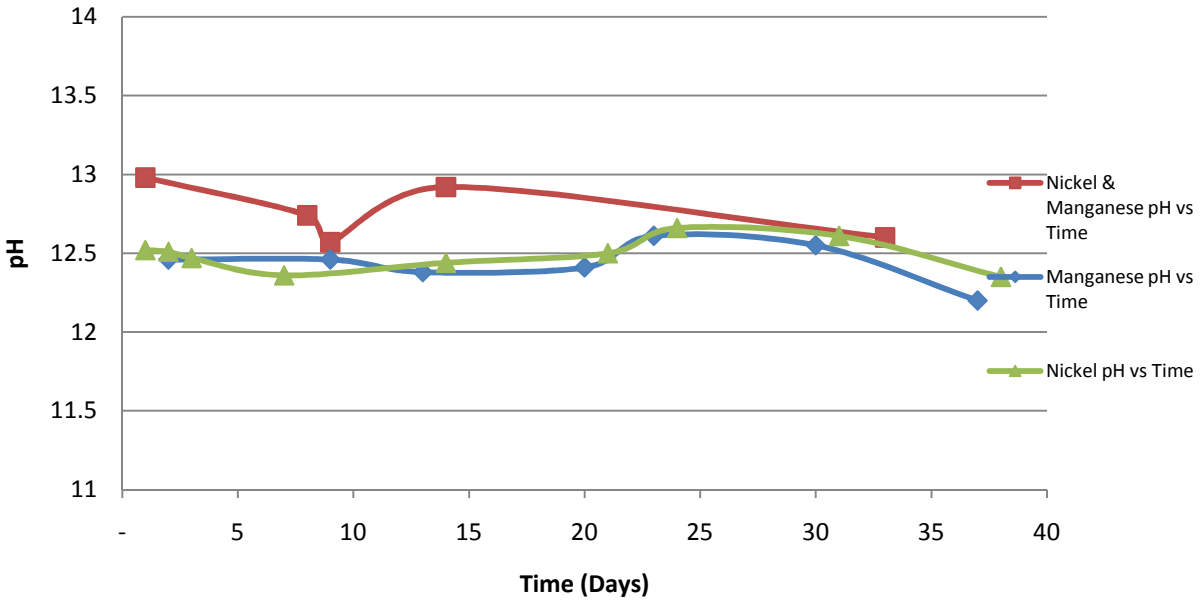


Figure 18 - Mixed nickel and manganese precipitated from 100 mL of 5 g/L nickel, 2g/L manganese in sulphate system with 5 mL additions of 28.58 g/L NaOH, nickel precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH & manganese precipitated from 100 mL of 2 g/L manganese in sulphate system with 5 mL additions of 8.58 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), pH vs Time

Figure 18 shows that the nickel and manganese hydroxide precipitation experiments did no undergo any distinct pH shift over time.

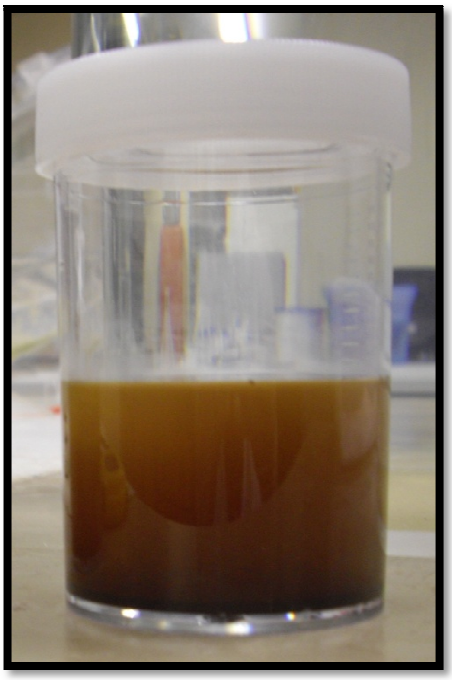


Figure 19 – Image of manganese freshly precipitated from 100 mL of 2 g/L manganese in sulphate system with 5 mL additions of 8.58 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

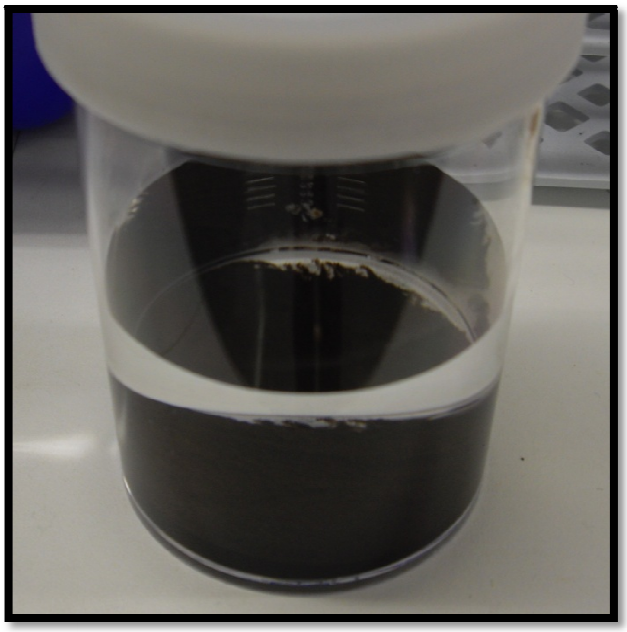


Figure 20 - Image of manganese aged 2 days, precipitated from 100 mL of 2 g/L manganese in sulphate system with 5 mL additions of 8.58 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

Figure 19 and Figure 20 show the manganese precipitate over time. The manganese probably only forms small amounts of manganese hydroxide before it oxidises into Mn_3O_4.

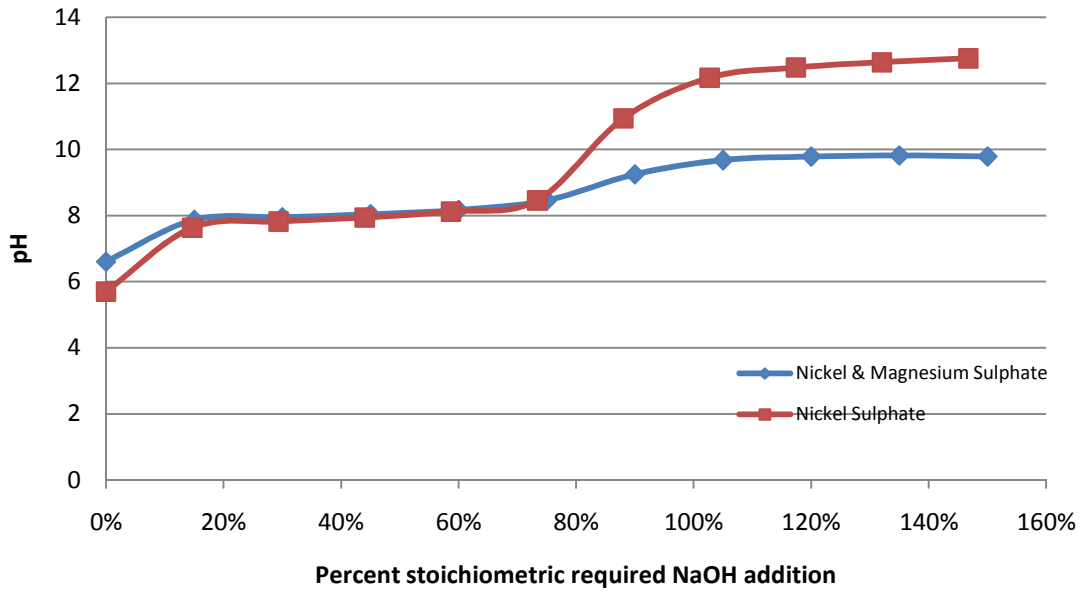


Figure 21 - Mixed nickel and magnesium precipitated from 100 mL of 5 g/L nickel, 10 g/L manganese in sulphate system with 5 mL additions of 20 g/L NaOH, nickel precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), NaOH addition vs pH.

* The hydroxide addition was not modified between the plain nickel and mixed nickel and magnesium experiments as complete magnesium precipitation was not desired.

Figure 21 shows that with magnesium in the system, there appears to be two distinct precipitation stages. The first was between pH 7.8 and 8.1, completing the precipitation stage when only 75-90% of the required hydroxide was added. The second was between pH 9.0-10.0 where the remaining hydroxide additions were consumed. The first stage appears just like plain nickel precipitation, indicating that the nickel may be precipitating independently of the presence of magnesium.

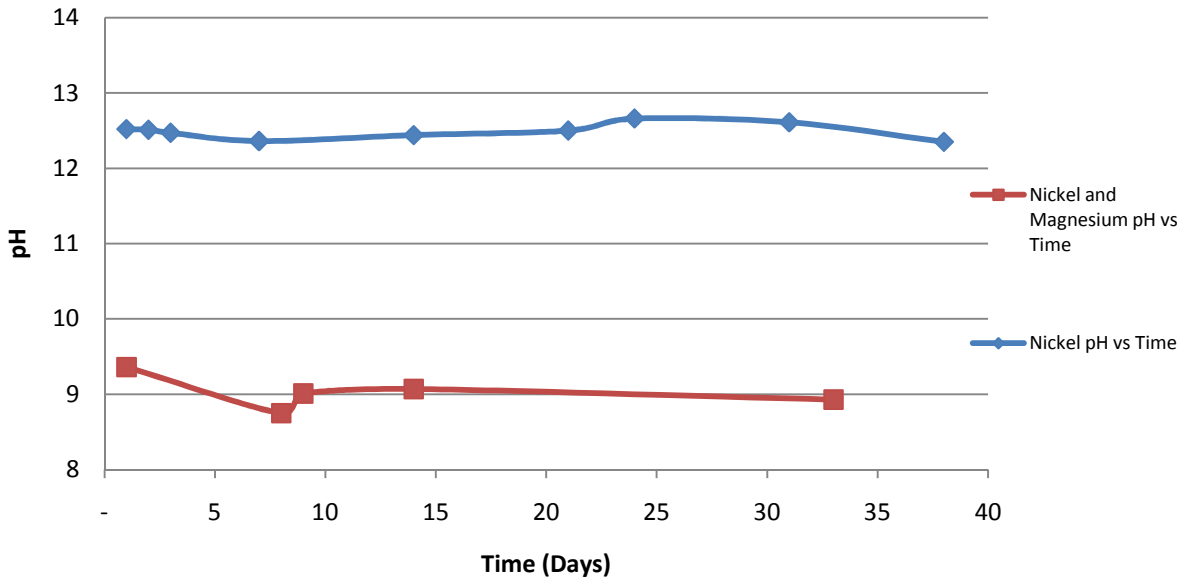


Figure 22 - Mixed nickel and magnesium hydroxide precipitated from 100 mL of 5 g/L nickel, 10 g/L manganese in sulphate system with 5 mL additions of 20 g/L NaOH, nickel hydroxide precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), pH vs Time

* The hydroxide addition was not modified between the plain nickel and mixed nickel and magnesium experiments as complete magnesium precipitation was not desired.

Figure 22 shows that the nickel and manganese hydroxide precipitation experiments underwent some hydroxide concentration drop over time. This could have been because the magnesium was not completely precipitated when the titration was completed to 150% of the hydroxide addition require to form complete nickel hydroxide.

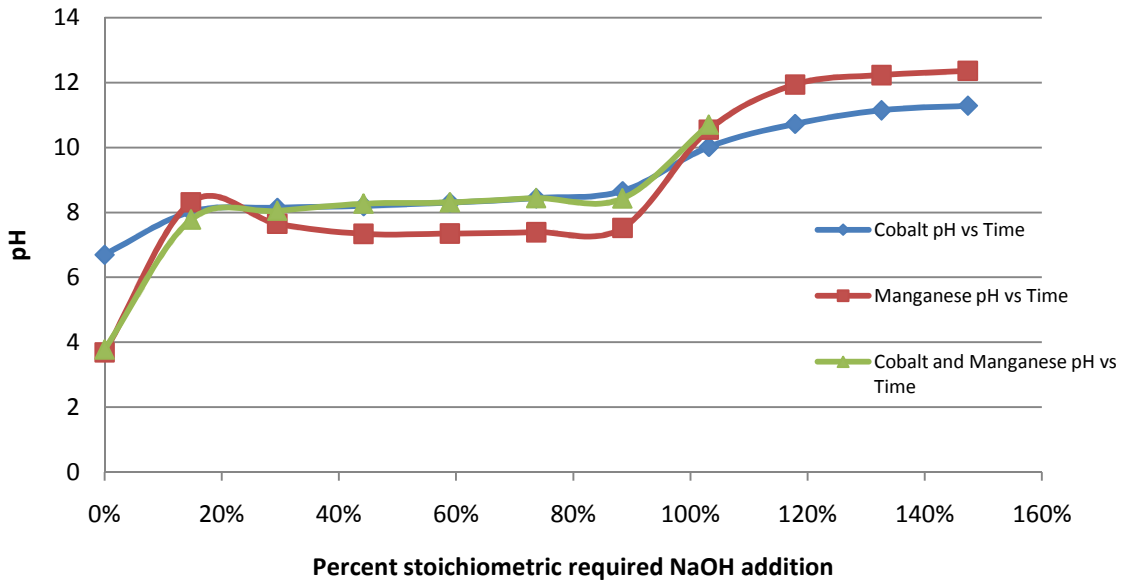


Figure 23 - Mixed cobalt and manganese precipitated from 100 mL of 0.5g/L cobalt and 2 g/L manganese in sulphate system with 5 mL additions of 10.58 g/L NaOH*, cobalt precipitated from 100 mL of 0.5g/L cobalt in sulphate system with 5 mL additions of 2 g/L NaOH & manganese precipitated from 100 mL of 2 g/L manganese in sulphate system with 5 mL additions of 8.58 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), NaOH addition vs pH

* The various extent titration experiment results were used for this plot. As such, comparing the pH over time is not applicable because the titrations finished at different points.

Figure 23 shows that the mixed cobalt and manganese system appears to follow the cobalt titration curve. The precipitation stage occurs between pH 7.8 and 8.2 and completing when 90-105% of the required hydroxide was added.

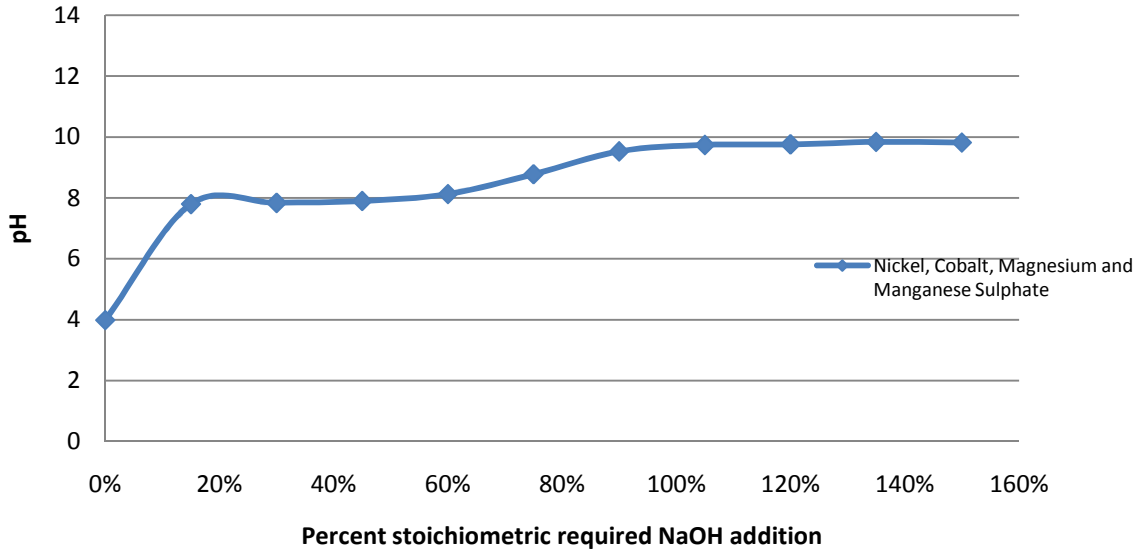


Figure 24- Mixed Nickel, cobalt, manganese and magnesium precipitated from 100 mL of 5g/L nickel, 0.5g/L cobalt 2 g/L manganese and 10g/L magnesium in sulphate system with 5 mL additions of 30.58 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), NaOH addition vs pH

Table 9 summarises the complete titration experimental results.

Table 9 – Summary of complete titration experimental results

Metal Hydroxide	Precipitates at pH	% Hydroxide consumption	Over Time
Nickel Hydroxide	7.8-8.1	75-90%	pH remains steady
Nickel Hydroxide 50 °C	7.8-8.1	75-90%	pH remains steady
Nickel Hydroxide 80 °C	7.8-8.1	90-105%	pH remains steady
Cobalt Hydroxide	8.0-8.2	90-105%	pH drops significantly
Manganese Hydroxide	Initially 8.2 then drops to 7.2	90-105%	pH remains steady
Nickel & Cobalt Hydroxide	7.8-8.1, same as plain nickel	75-90%, same as plain nickel	pH remains steady
Nickel & Manganese Hydroxide	7.8-8.1, same as plain nickel	75-90%, same as plain nickel	pH remains steady
Nickel and Magnesium Hydroxide	7.8-8.1 then 9.0-10.0	75-90%	pH remains steady

Cobalt and Manganese Hydroxide	8.0-8.2, same pH as plain cobalt	90-105%	N/A
Nickel, Cobalt, Manganese and Magnesium	7.8-8.1		

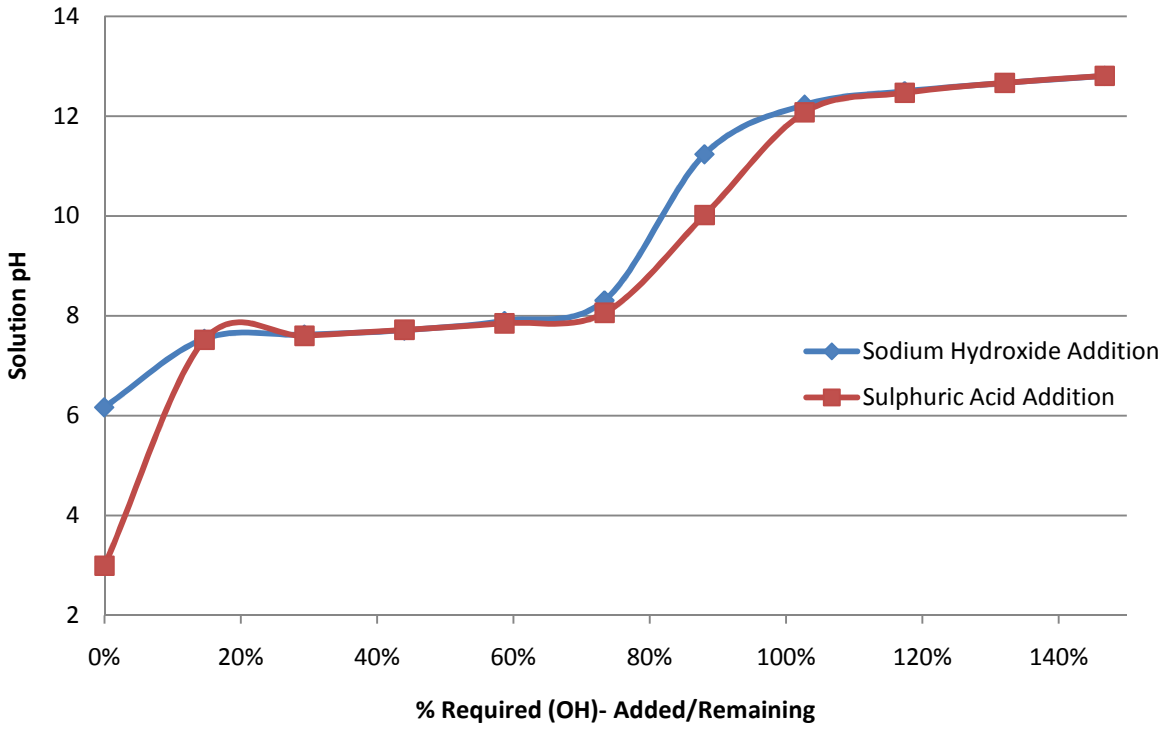


Figure 25 - Nickel hydroxide precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), then reverse titrated using 5 mL additions of 25.07 g/L sulphuric acid, pH vs % OH added/remaining

The sulphuric acid addition rate was calculated to be equal and opposite to the hydroxide rate assuming that all of the sulphuric acid dissociated.

Figure 25 shows that both the nickel hydroxide precipitation and dissolution occurred between pH 8.1 and 7.8. Throughout the precipitation stage both the precipitation and dissolution pH measurements line up almost exactly.

6.1.2 **Settling Rate Results**

Observing the precipitate formed from the complete titration experiments gave information on the settling rates.

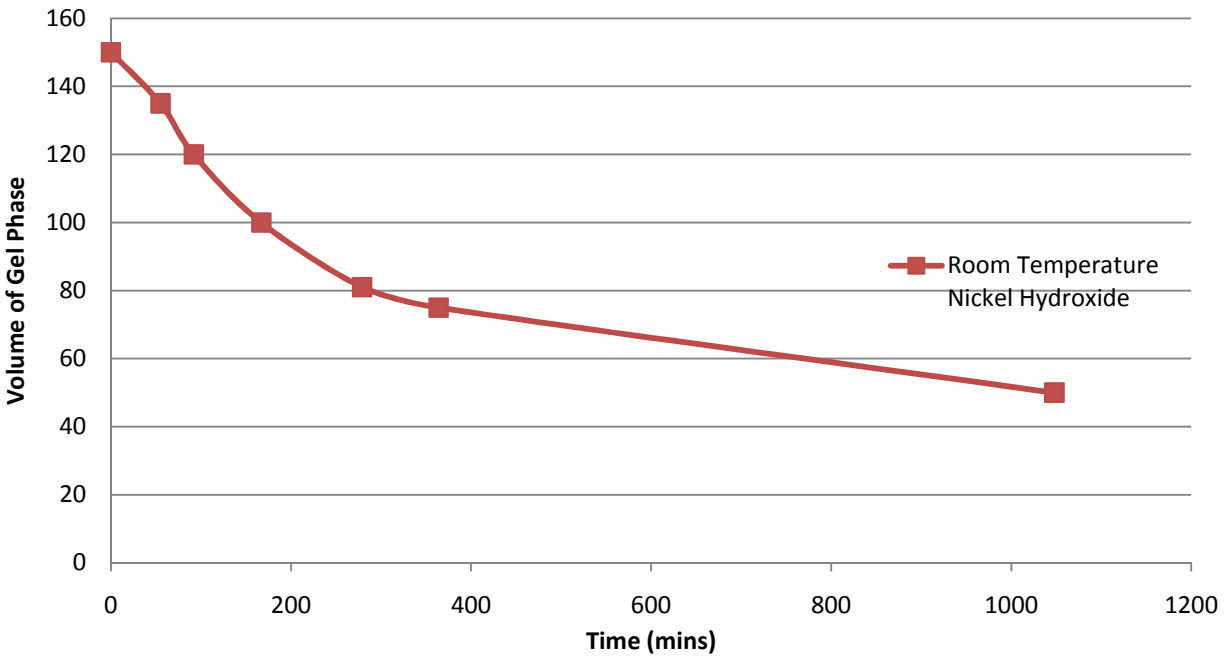


Figure 26 - Nickel hydroxide precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), volume of gel-like phase vs time

Figure 26 shows that the nickel hydroxide precipitated at room temperature has an incredibly slow rate of settling, with 5 g/L nickel as the hydroxide taking over 17 hours to settle to a third of its original volume.

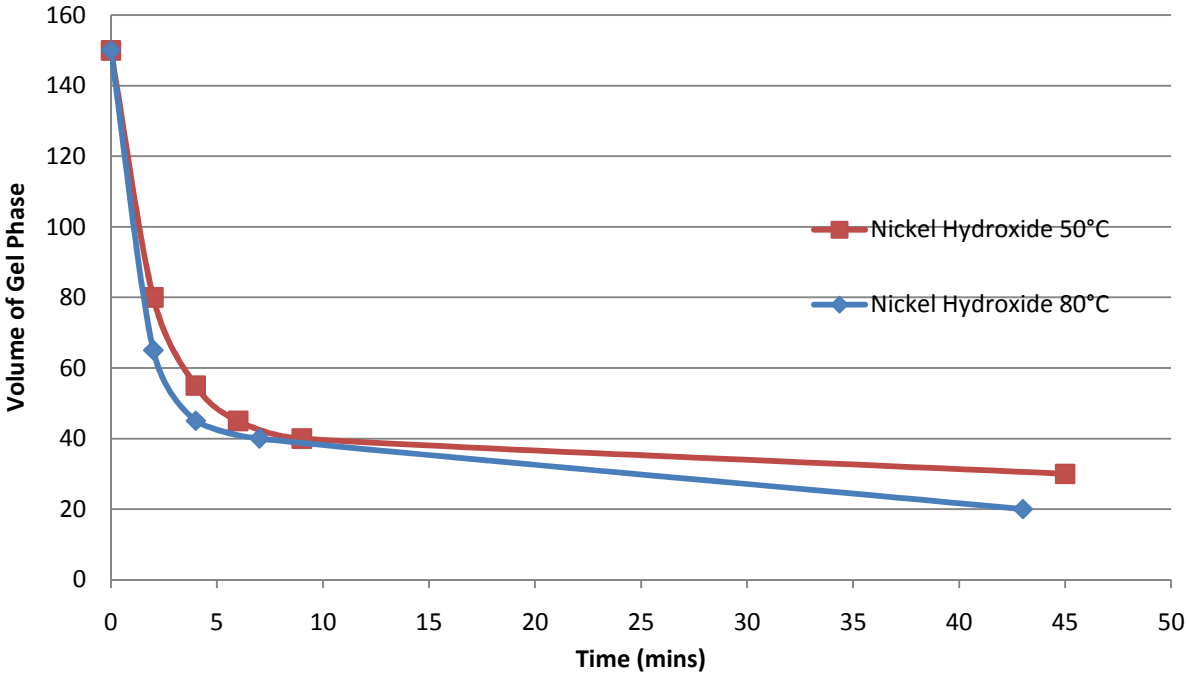


Figure 27 - Nickel hydroxide precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at 50 °C and 80 °C, volume of gel-like phase vs time

Figure 27 shows that the nickel hydroxide precipitated at higher temperatures was found to have much more favourable settling properties.

Nickel hydroxide precipitated between pH 7.9 and 8.1 irrespective of the system temperature. The major differences between the nickel hydroxide precipitation at room temperature, 50 °C and 80dC were the apparent hydroxide intake and the settling rate. Both the room temperature and 50 °C systems seemed to completely precipitate when only 70-80% of the hydroxide required to form the complete metal hydroxide solid was added. The 80 °C system completed precipitation when 100% of the required hydroxide was added. This indicates that the room temperature and 50 °C precipitates are chemically more similar than the 80 °C precipitate. Interestingly, the settling rates for the two elevated temperature precipitations were very similar while the room temperature sample settling was much slower. This indicates that the hydroxide consumption is not a major factor affecting the settling rate. But is also indicates that the precipitate formed at 80 °C is chemically different to the precipitate formed at lower temperatures. It must be noted that both the room temperature and the 80 °C experiments were carried out using magnetic stirring and in the case of the 80 °C sample, a hot plate. The 50 °C

samples on the other hand were carried out in the oven which shook the samples at approximately 100 rpm.

6.1.3 Filtered Metal Hydroxides

Figure 28, Figure 29, Figure 30, Figure 31 and Figure 32 show the effect of aging on the filtered nickel hydroxide. The filter cake appeared to shrink and curl up as time passed and it went slightly transparent. Condensation was observed on the Petri dish lid. The cake was very brittle and shattered into a number of pieces when handled.

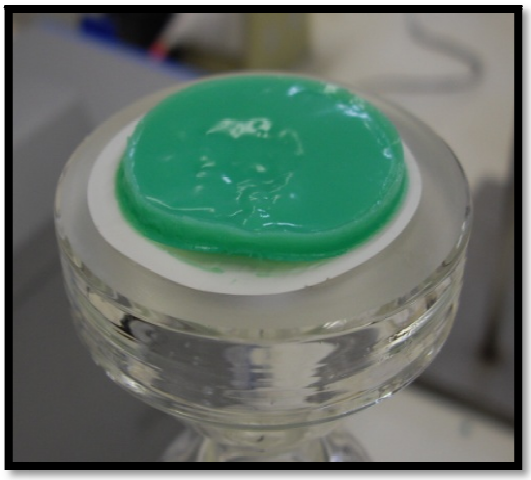


Figure 28 –Nickel hydroxide immediately after filtering on 0.2 micron filter paper, precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

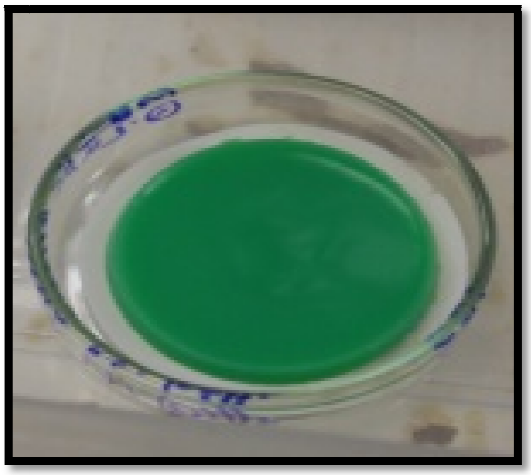


Figure 29– Nickel hydroxide filtered on 0.2 micron filter paper and aged approximately 2 hours, precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

Figure 30 –Nickel hydroxide filtered on 0.2 micron filter paper and aged 1 day, precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

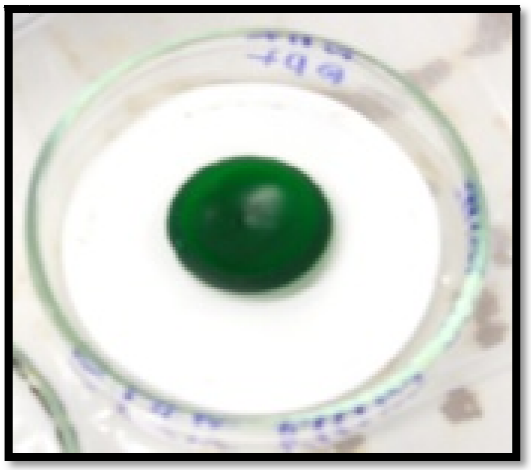


Figure 31–Nickel hydroxide filtered on 0.2 micron filter paper and aged 2 days, precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

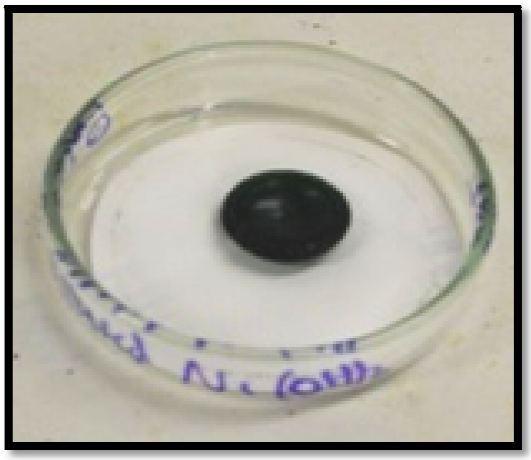


Figure 32 –Nickel hydroxide filtered on 0.2 micron filter paper and aged 30 days, precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

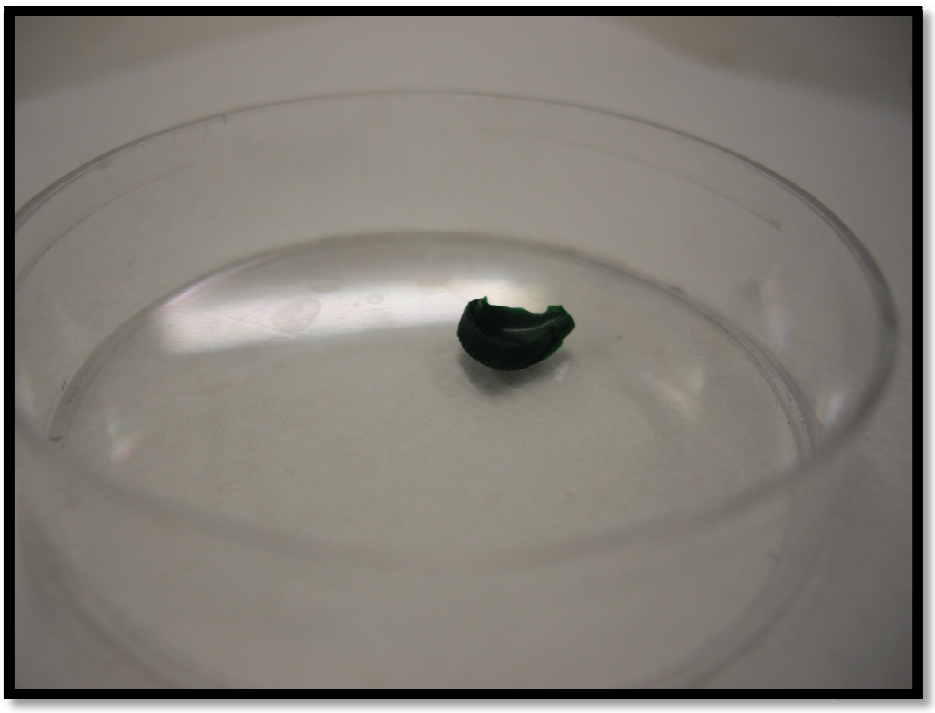


Figure 33 – A piece of nickel hydroxide filtered on 0.2 micron filter paper and aged >30 days, precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

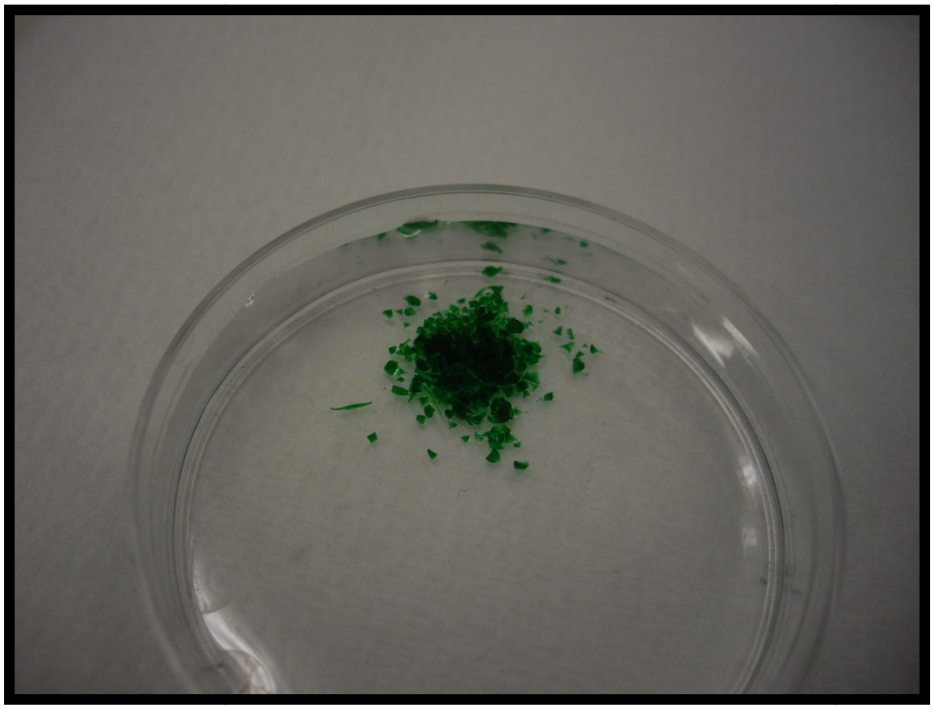


Figure 34 - A piece of nickel hydroxide filtered on 0.2 micron filter paper and aged >30 days, precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), after submerging in distilled water

Figure 33 shows a piece of the aged nickel hydroxide cake. Distilled water was added to the Petri dish and the piece of aged nickel hydroxide cake was observed to shatter into a number of pieces within the space of a minute. The same piece of filter cake is shown in Figure 34 approximately 2 minutes after being submerged in distilled water. There is obviously some very high energy reaction going on to force the shards to eject from the filter cake so violently.

6.1.4 **Particle Sizing**

Three samples of the nickel hydroxide precipitate were sent to Matec Applied Science in America to be particle sized. The three samples were:

- Nickel hydroxide freshly precipitated at room temperature
- Nickel hydroxide precipitated at room temperature and aged 1 month
- Nickel hydroxide precipitated at 80 °C and aged 1 month

At the time of writing, MAS had not completed the particle size analysis.

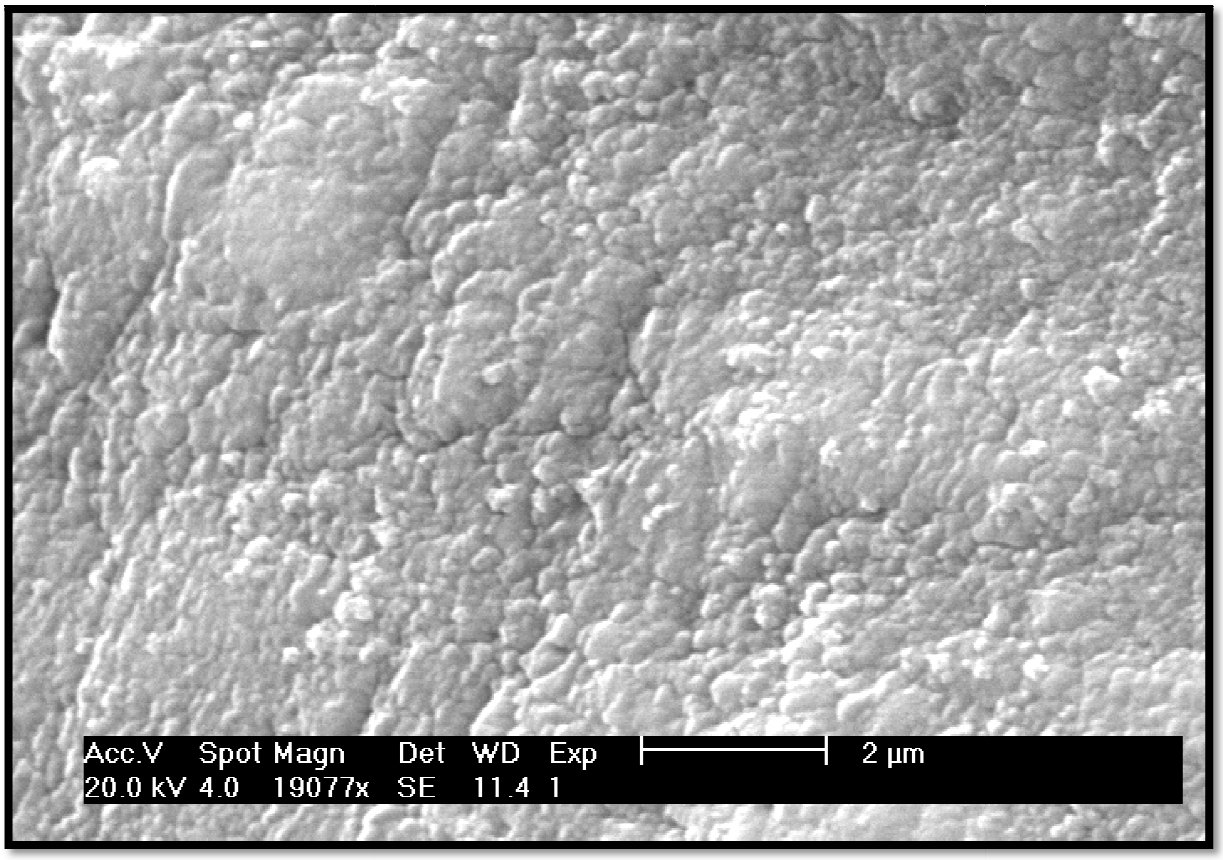


Figure 35 – SEM image of freshly filtered nickel hydroxide precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

Figure 35 shows an SEM image of some of the nickel hydroxide cake which was platinum coated in a vacuum approximately 1 day after being filtered. The sample was to be platinum coated under vacuum in order to remove any free water and prepare for the SEM analysis. The image shows no sign of individual particles on the scale of 1 micron and the surface appears rather flat and unstructured.

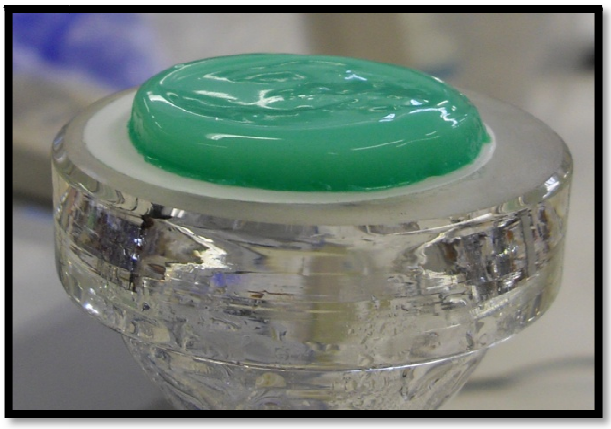


Figure 36 –Nickel hydroxide aged >30 days is shown immediately after filtering on 0.2 micron filter paper, precipitated from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at 50 °C

The top of the filter cake shown in Figure 36 was much wetter than expected despite being vacuum filtered. On closer inspection it was noted that the cake immediately touching the filter paper was very dry suggesting that the top part of the cake could not filter because the lower section was not allowing sufficient water flow.

Figure 37 – Cobalt precipitate aged > 30 days is shown immediately after filtering on 0.2 micron filter paper, precipitated from 100 mL of 0.5 g/L cobalt in sulphate system with 5 mL additions of 2 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

The cobalt precipitate filter cake shown in Figure 37 appears to be comprised of fine particulates.

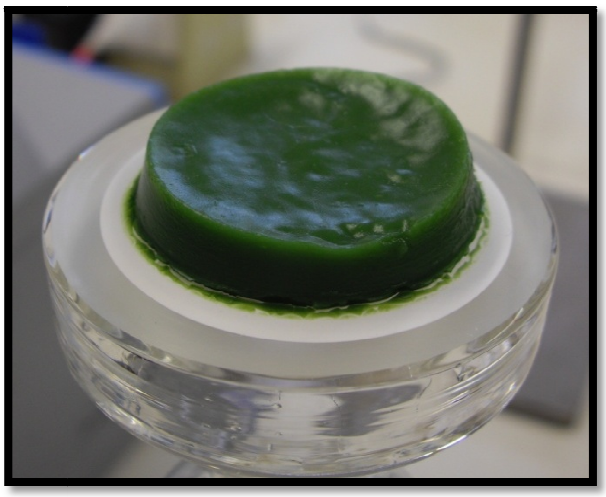


Figure 38–Nickel and cobalt hydroxide aged > 30 days is shown immediately after filtering on 0.2 micron filter paper, precipitated from 100 mL of 5 g/L nickel and 0.5 g/L cobalt in sulphate system with 5 mL additions of 22 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

The mixed nickel and cobalt hydroxide filter cake shown in Figure 38 has a much larger volume than the individual nickel and cobalt filter cakes.

6.1.5 Calculations

The decanted nickel hydroxide solution and the other metal hydroxide filter cakes were weighed in order to calculate the hydration factor. Table 10 shows the results along with the calculated hydration factors. These values were calculated assuming that all of the metal in solution was precipitated as the $M(OH)_2$ and that the excess mass measured from the samples was due to hydration.

Table 10 – Calculated hydration factors

	Measured mass of phase	Assumed mass of metal hydroxide	Remaining mass assumed as water	Molecular hydration factor
Decanted Nickel Hydroxide at room temperature	35.00	0.79	34.21	223
Filtered Nickel Hydroxide at room temperature	4.61	0.79	3.82	25
Filtered Nickel Hydroxide at 50 ℃	6.71	0.79	5.92	39
Filtered aged 4 days Nickel Hydroxide at room temperature	3.63	0.79	2.84	19
Filtered Cobalt Hydroxide at	0.70	0.08	0.62	40

room temperature				
Filtered aged 4 days Cobalt Hydroxide at room temperature	7.66	1.58	6.08	20
Filtered Nickel & Cobalt Hydroxide at room temperature	8.55	0.87	7.68	46

These hydration factors give indication as to the number of water molecules surrounding each hydroxide molecule. They are decanted nickel hydroxide hydration is very high, showing that the gel-like phase is highly dispersed even once it was settled.

6.2 Various Extent Titration Experiments

6.2.1 UV Vis Spectra Results

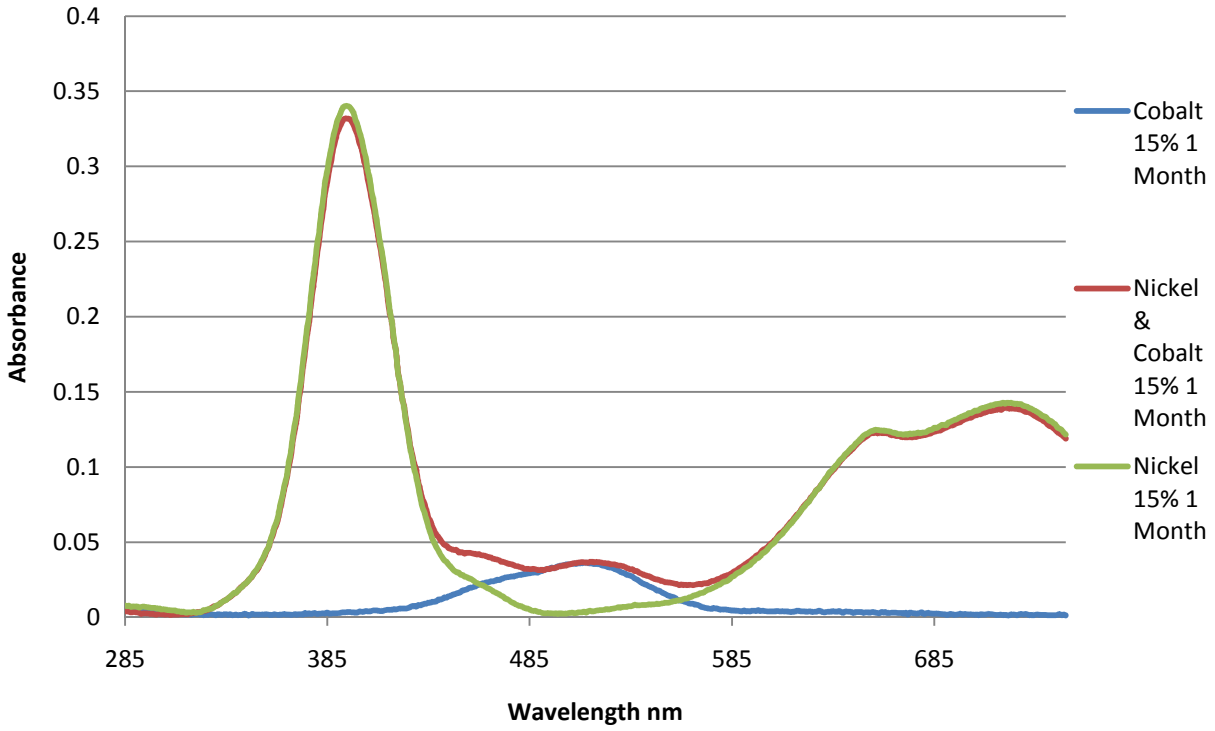


Figure 39 – UV Vis spectroscopy absorbance analysis on nickel, cobalt and mixed nickel and cobalt systems precipitated to 15% of hydroxide requirement from 100 mL samples containing 5 g/L nickel and/ or 0.5 g/L cobalt in sulphate, with 5 mL additions of 20, 2 and 22 g/L NaOH respectively, titrated every 30 minutes at room temperature (~22 °C)

Figure 39 shows the UV-Vis spectra of nickel, cobalt and mixed nickel and cobalt samples. Work by Olveira, Finazzi and Carlos (2006) indicates that the peaks at 395 nm, 655 nm and 720 nm relate to the hexaaquanickel ion although there is no indication on whether the ion is in multiple conformations. (Oliveira, Finazzi & Carlos 2006)

Little information regarding the cobalt spectra could be obtained so it can only be assumed that the minor peaks at 470 nm and 513 nm relate to cobalt complexation.

6.2.2 AAS Results

The various extent titration experiments were analysed for pH and sampled one day, one week and one month after the titration was carried out.

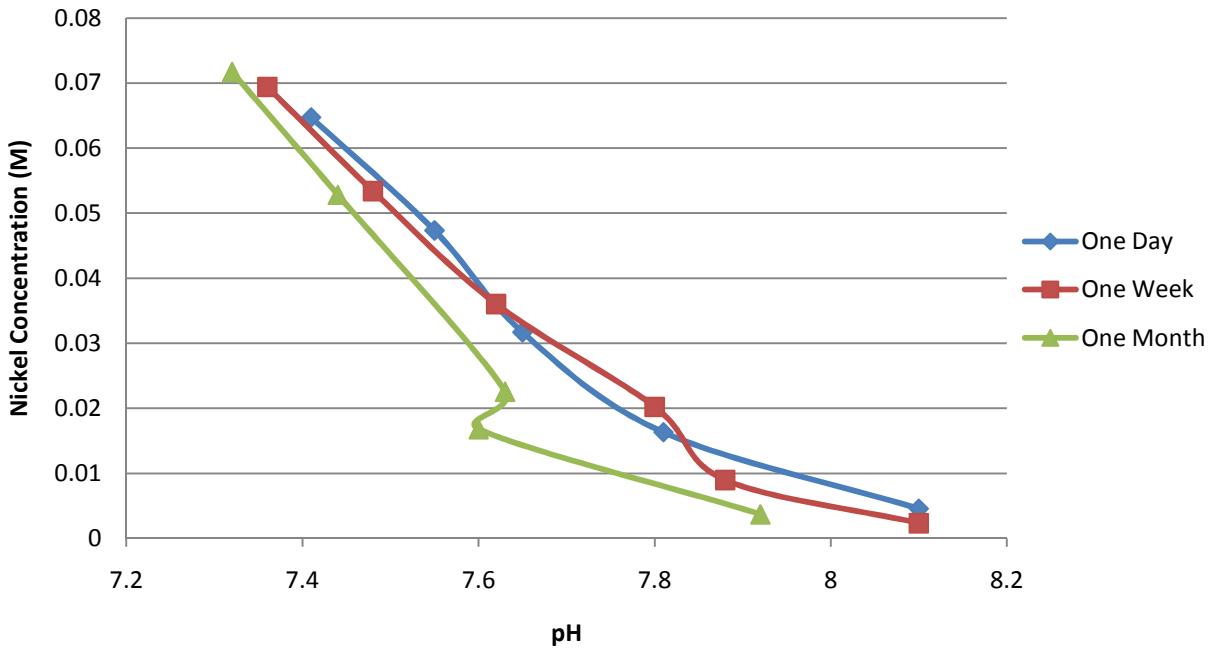


Figure 40 – Nickel hydroxide precipitated to various extents from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), pH vs nickel concentration over time

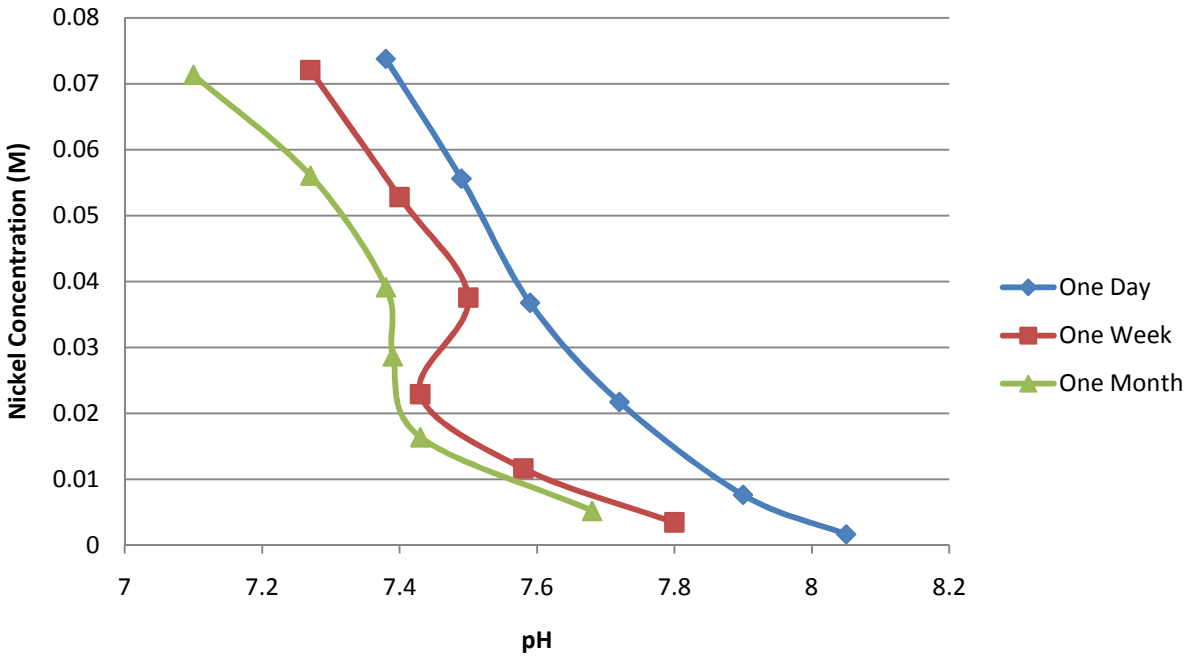


Figure 41 – Nickel hydroxide precipitated to various extents from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at 50 °C, pH vs nickel concentration over time

Figure 40 and Figure 41 show the pH vs nickel concentrations for nickel hydroxide system s precipitated at room temperature and 50 °C over time. The systems precipitated at room temperature and 50 °C both underwent the same type of nickel concentration and pH shift over time although the higher temperature systems changed to a greater extent. In both, the pH decreases over time with the room temperature samples pH decreased by approximately 0.1-0.2 over the month while the 50 °C samples pH decreased by approximately 0.4. The nickel concentrations in the room temperature samples remained relatively constant while to the lower nickel concentrations in the 50 °C samples increased slightly and the higher concentrations remained relatively constant.

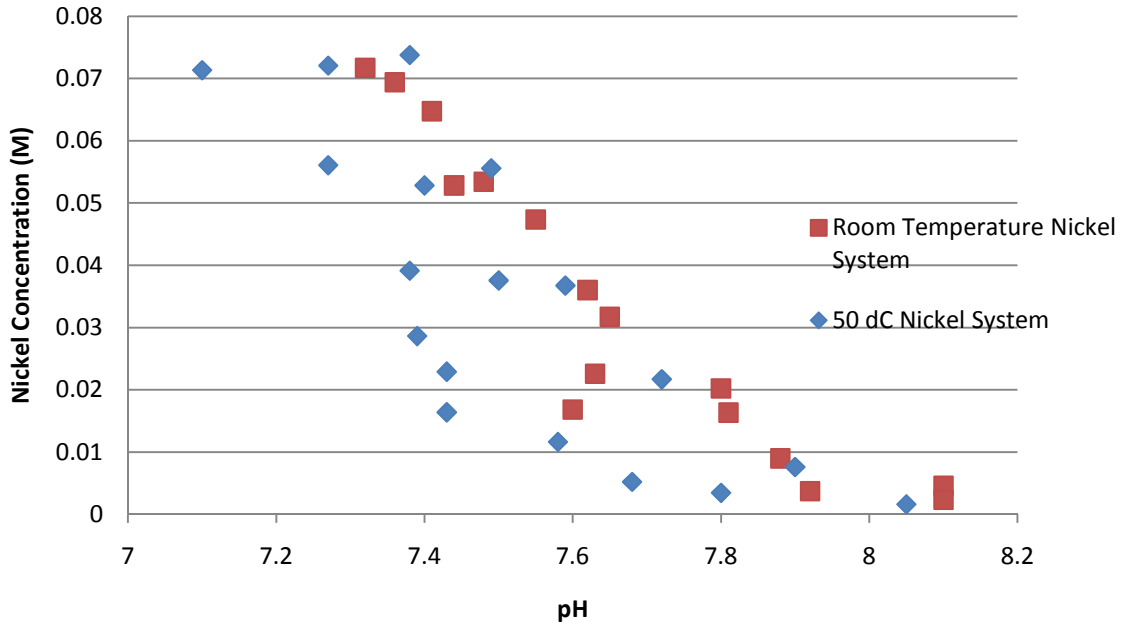


Figure 42 - Nickel hydroxide precipitated to various extents from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C) and 50 °C, pH vs nickel concentration

Figure 42compares the room temperature and 50 °C nickel hydroxide equilibrium conditions. While both hot and room temperature system s initially have the same pH vs nickel concentration conditions, over time the pH of the 50 °C samples drops significantly such that at the same concentration, the nickel hydroxide precipitated at 50 °C can be found at a lower pH.

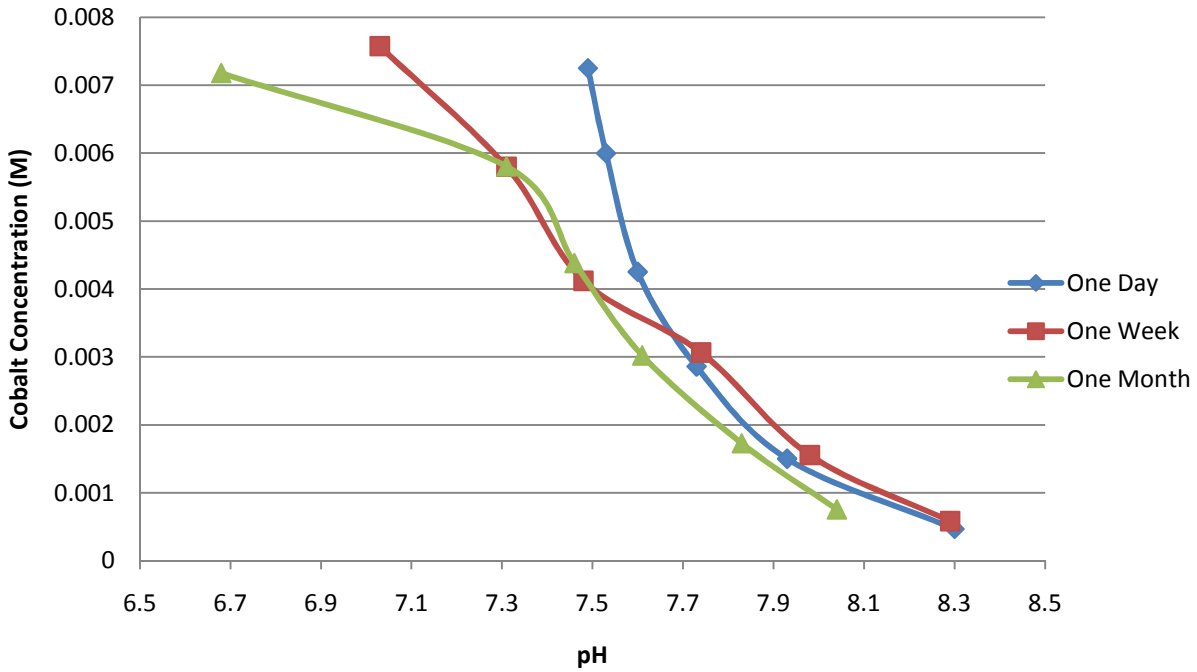


Figure 43– Cobalt hydroxide precipitated to various extents from 100 mL of 0.5 g/L cobalt in sulphate system with 5 mL additions of 2 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), pH vs cobalt concentration over time

Figure 43 shows the pH vs cobalt concentrations over time for cobalt hydroxide system s precipitated at room temperature. Over the month the pH in these systems decreased with the lower concentration systems decreasing much less than the higher concentrated systems. That is, when there is lots of cobalt in solution the pH drops significantly over time although the cobalt concentration does not vary significantly. This could be due to cobalt complexing with the hydroxide in solution such that when the pH is measured, the complexed hydroxide is not taken into account but when the sample is AAS analysed, the complexed cobalt is measured. Furthermore, the cobalt Eh pH diagram given back in the literature review showed that at cobalt hydroxyl complexes are the most stable cobalt species below pH 6, rather than cobalt aqua complexes.

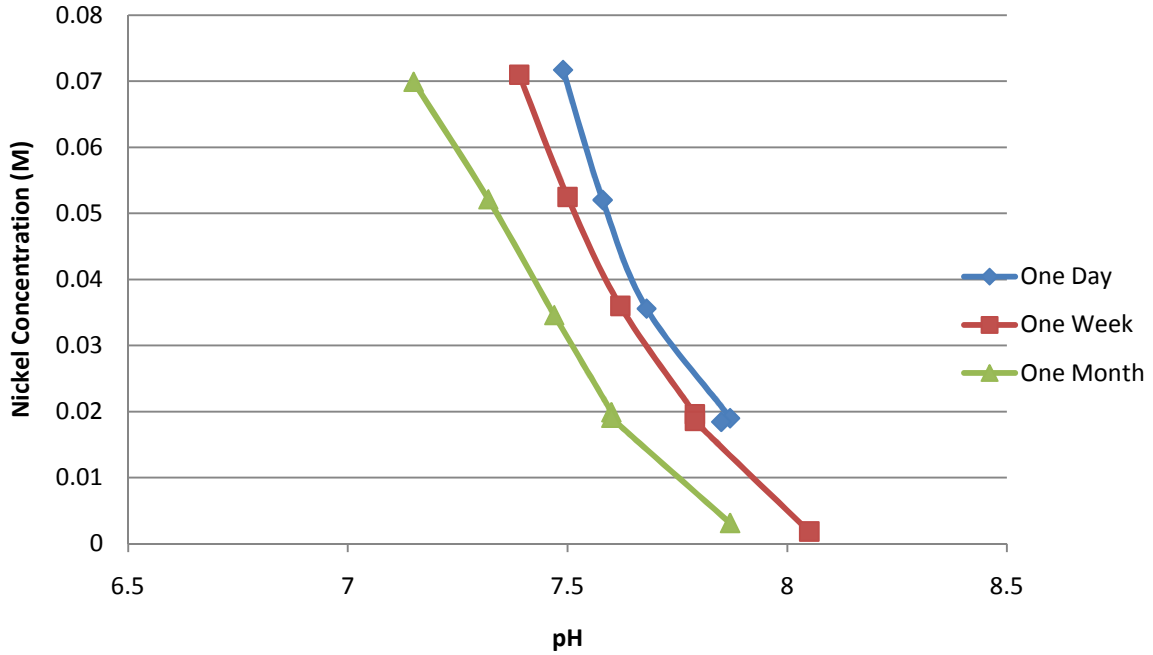


Figure 44 – Mixed nickel and cobalt hydroxide precipitated to various extents from 100 mL of 5 g/L nickel and 0.5 g/L cobalt in sulphate system with 5 mL additions of 22 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), pH vs nickel concentration over time

The pH of the nickel systems drops steadily over time with very little change in the nickel concentration. The pH shift with respect to time shown in this graph does not appear to depend on the nickel concentration which indicates that nickel complexing with the hydroxide is not causing the measured pH drop. Instead it would appear that the nickel hydroxide is simply absorbing more hydroxide ions into the phase. Although one would assume that the rate of hydroxide absorption into the nickel hydroxide phase would be proportional to the mass of nickel hydroxide precipitated. This is clearly not the case as a large mass of nickel hydroxide is precipitated when the measured nickel concentration is low.

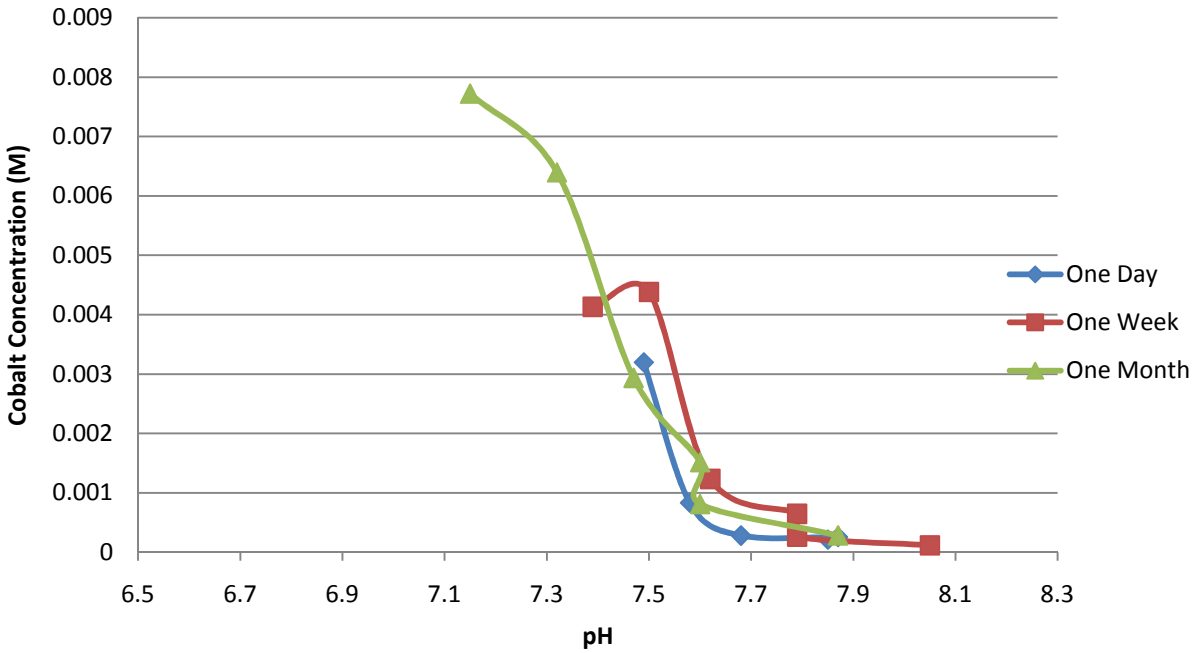


Figure 45 – Mixed nickel and cobalt hydroxide precipitated to various extents from 100 mL of 5 g/L nickel and 0.5 g/L cobalt in sulphate system with 5 mL additions of 22 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), pH vs cobalt concentration over time

Figure 45 shows how the high concentrations of cobalt only exist once the system is aged for a month indicating that it all precipitated when the titration was run and over the month it redissolved into the solution.

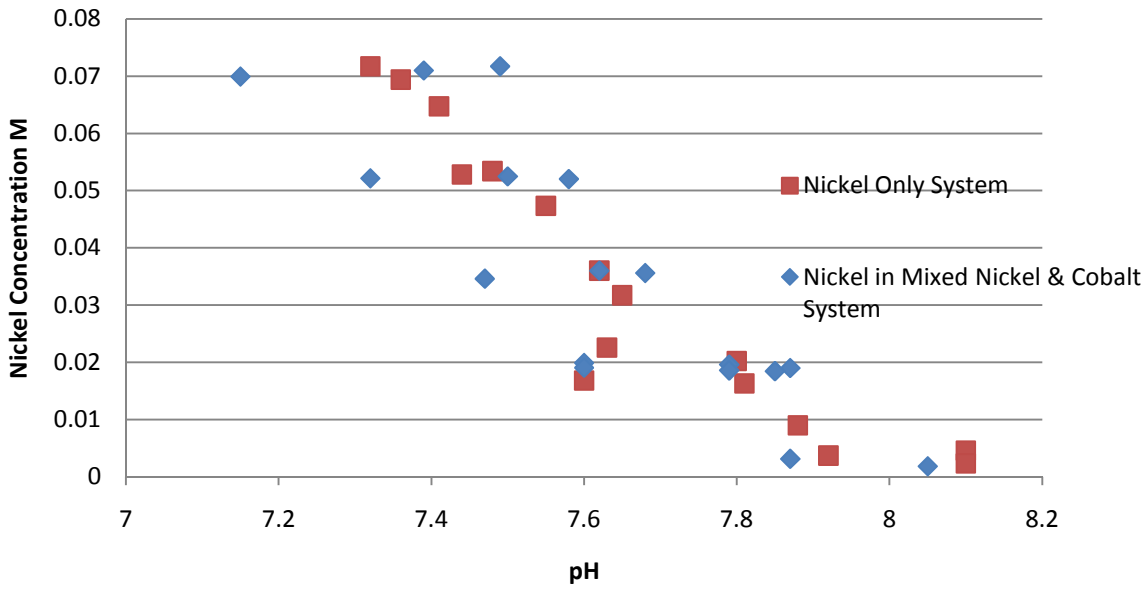


Figure 46 – Mixed nickel and cobalt hydroxide precipitated to various extents from 100 mL of 5 g/L nickel and 0.5 g/L cobalt in sulphate system with 5 mL additions of 22 g/L NaOH and nickel hydroxide precipitated to various extents from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), pH vs nickel concentration

The effect of cobalt in solution on the nickel precipitation appears to cause the nickel to precipitate within a much tighter pH range.

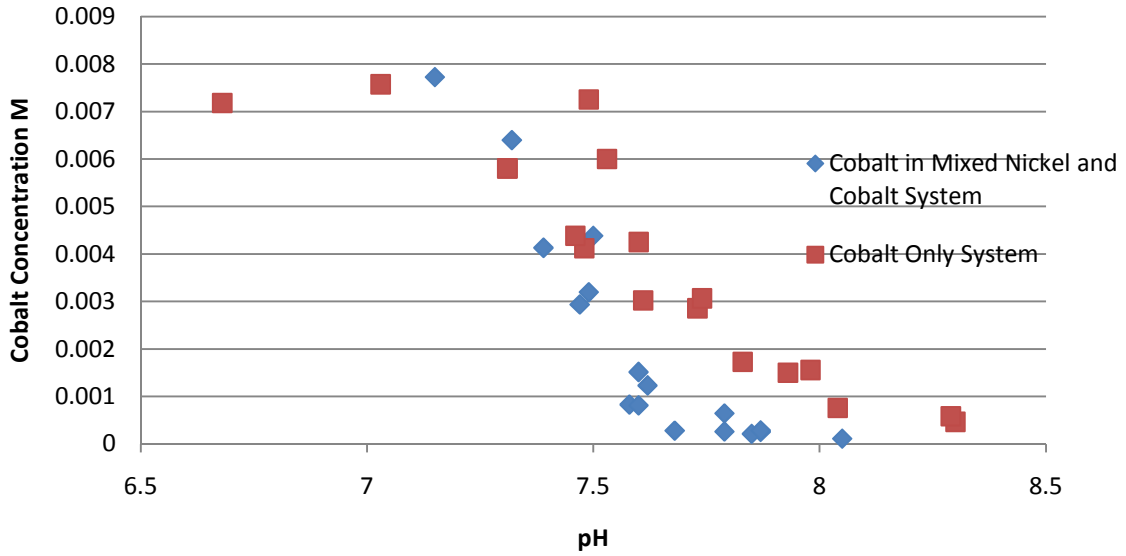


Figure 47 – Mixed nickel and cobalt hydroxide precipitated to various extents from 100 mL of 5 g/L nickel and 0.5 g/L cobalt in sulphate system with 5 mL additions of 22 g/L NaOH and cobalt hydroxide precipitated to various extents from 100 mL of 0.5 g/L cobalt in sulphate system with 5 mL additions of 2 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C), pH vs cobalt concentration

Figure 47 clearly shows that nickel makes cobalt precipitate at lower pH.

6.2.3 Calculations

The pH and metal concentrations measured in each of the various extent titration experiments was used to carry out calculations regarding the equilibrium between the metal, the hydroxide ions and the precipitate.

All calculations were carried out assuming that the 2+ metal ion reacts with 2 hydroxide ions to form the solid $M(OH)_2$. The assumed nickel and cobalt reactions are given in Equation 18 and Equation 19 respectively.

Equation 18 – Nickel hydroxide formation reaction

$$Ni^{2+} + 2OH^- \leftrightarrow Ni(OH)_2(s)$$

Equation 19 – Cobalt hydroxide formation reaction

$$Co^{2+} + 2OH^- \rightarrow Co(OH)_2(s)$$

As the metal and hydroxide concentrations were known, the equilibrium constant of the relevant metal hydroxide formation reaction could be calculated as per Equation 20 and Equation 21. These equations were developed assuming that the activity of the species was equivalent to the activity of the species, which is usually true at low concentrations, and that the activity of the solid species was one.

Equation 20 - Typical metal hydroxide formation reaction

$$M^{2+} + 2OH^{-} \leftrightarrow M(OH)_2(s)$$

Equation 21 - Typical metal hydroxide equilibrium product

$$K_{rxn} = \frac{1}{\left[M^{2+}\right]\left[OH^{-}\right]^2}$$

The calculated equilibrium products were averaged and summarised in Table 11.

Table 11 – Calculated metal hydroxide equilibrium constants

	Equilibrium constant, K_{rxn}
Room Temperature Nickel Hydroxide Precipitation	2.3E+14
50 °C Nickel Hydroxide Precipitation	4.7E+14
Room temperature nickel hydroxide precipitated from solution with cobalt hydroxide	2.7E+14
Room temperature cobalt hydroxide precipitate	5.5E+15
Room temperature cobalt hydroxide precipitated from solution with nickel hydroxide	6.4E+15

Once the reaction equilibrium constant for each reaction was known, it could be related to the free energy of reaction as described by Equation 11 in the literature review.

With the free energy of the reaction, the free energy of formation of the metal hydroxide could be approximated using Equation 12 given in the literature review. The free energy of formation

of the reactant species calculated from work carried out by Bard Parsons and Jordan (1985) and specified in Table 5 in the literature review were used to complete the free energy calculations.

Table 12 summarises the free energy of formation calculations and compares the calculated values with those sourced from literature for the crystalline precipitates.

Table 12 – Calculated metal hydroxide free energies of formation

	ΔG Formation kJ/mol
Room temperature nickel hydroxide precipitate	-442.0 ±2.5
50 °C nickel hydroxide precipitate	-443.3 ±2.0
Room temperature nickel hydroxide precipitated from solution with cobalt hydroxide	-442.0 ±2.5
Crystalline nickel hydroxide (Bard, Parsons & Jordan 1985)	-453
Room temperature cobalt hydroxide precipitate	-456.5 ±2.5
Room temperature cobalt hydroxide precipitated from solution with nickel hydroxide	-460.0 ±2.4
Crystalline cobalt hydroxide (Plyasunova, Zhang & Muhammed 1998)	-460.2 ±2.0

The free energies calculated for nickel hydroxide at room temperature, at 50 °C and at room temperature with cobalt are all very similar. The free energies of formation are also significantly higher than that of the crystalline nickel hydroxide specified by Bard, Parsons and Jordan (1985). This indicates that the gel-like nickel hydroxide phase is less stable than the crystalline phase. The cobalt hydroxide precipitated at room temperature was also calculated to have a slightly higher free energy of formation to the crystalline cobalt hydroxide specified by Bard, Parsons and Jordan (1985). Conversely, the cobalt hydroxide precipitated in the mixed nickel and cobalt system was calculated to have almost exactly the same free energy of formation as the crystalline phase. Clearly when the cobalt hydroxide is precipitated with nickel it is more stable than when precipitated alone.

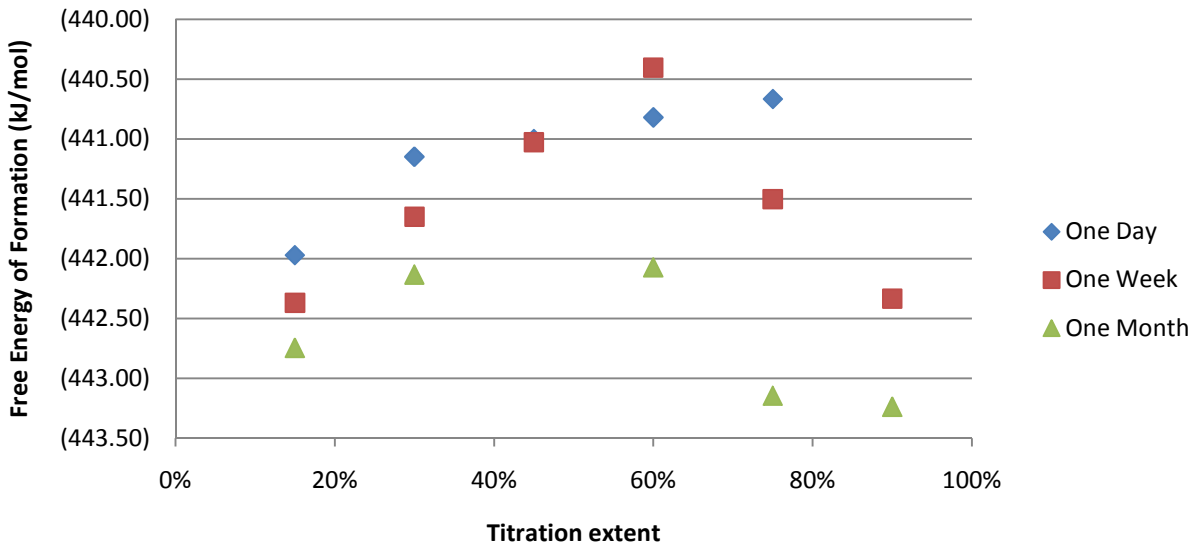


Figure 48 – Calculated free energy of formation of nickel hydroxide precipitated to various extents from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

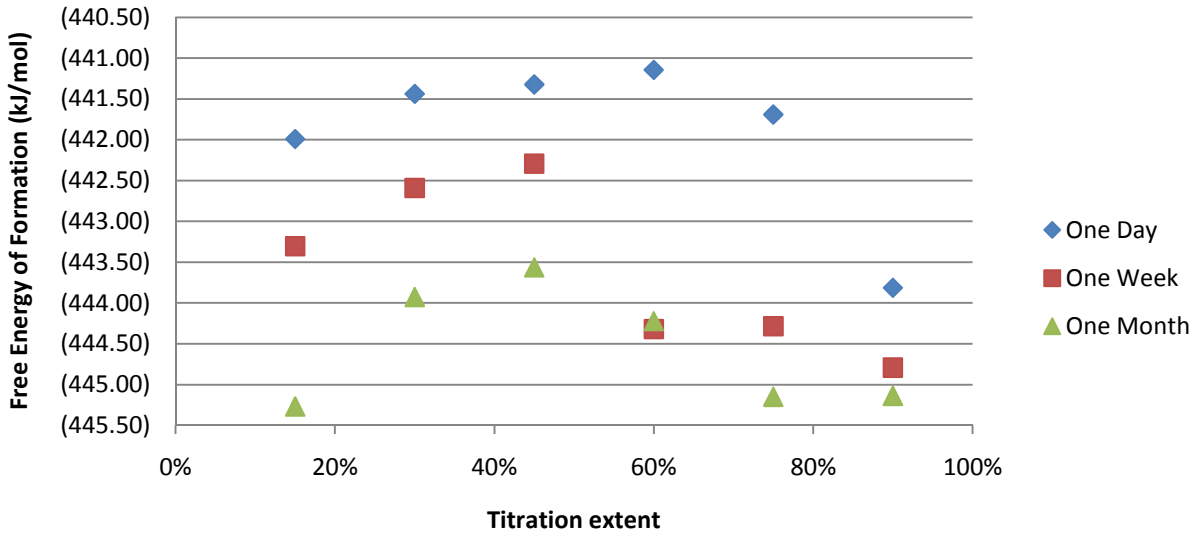


Figure 49 – Calculated free energy of formation of nickel hydroxide precipitated to various extents from 100 mL of 5 g/L nickel in sulphate system with 5 mL additions of 20 g/L NaOH, titrated every 30 minutes at 50 °C

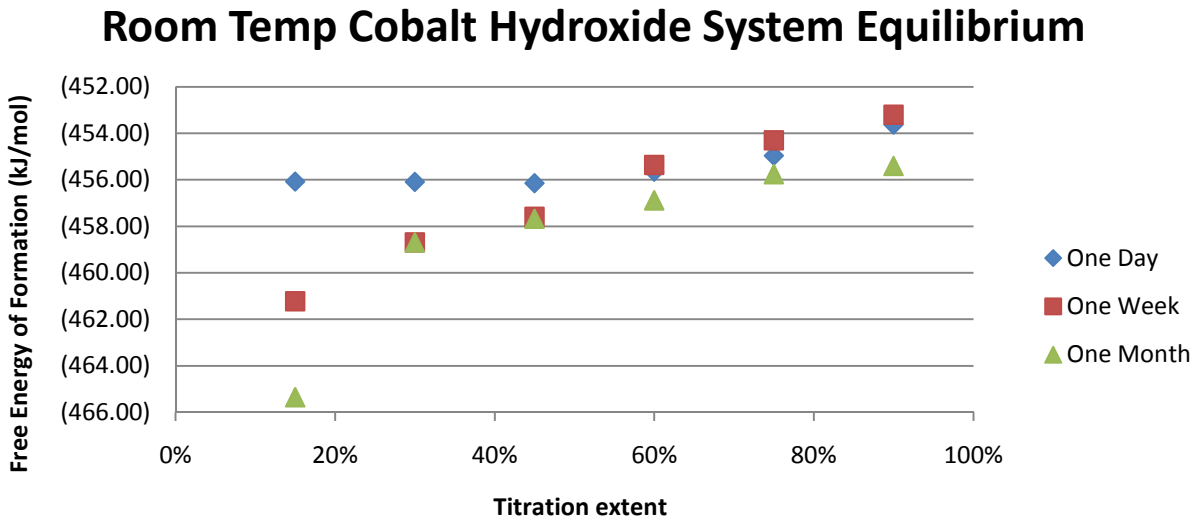


Figure 50 – Calculated free energy of formation of cobalt hydroxide precipitated to various extents from 100 mL of 0.5 g/L cobalt in sulphate system with 5 mL additions of 2 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

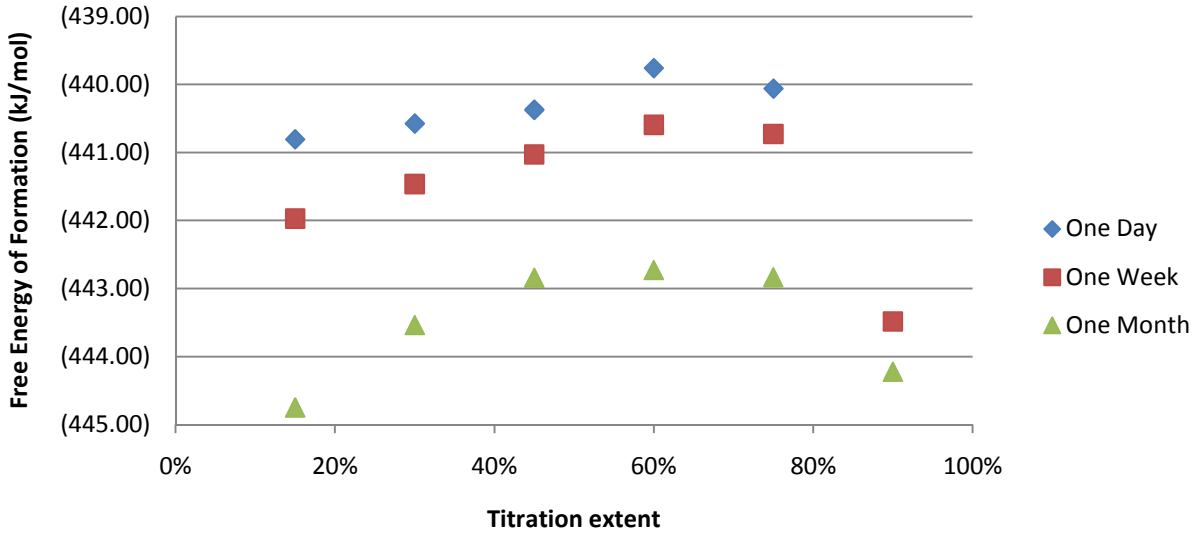


Figure 51 – Calculated free energy of formation of nickel hydroxide in a mixed nickel and cobalt hydroxide precipitated to various extents from 100 mL of 5 g/L nickel and 0.5 g/L cobalt in sulphate system with 5 mL additions of 22 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

Figure 48, Figure 49, Figure 50 Figure 51 clearly show that the respective precipitates were changing over time. All of the free energy calculations and hydroxide concentration

measurements noted previously indicated that the precipitates were slowly rearranging into a more stable phase.

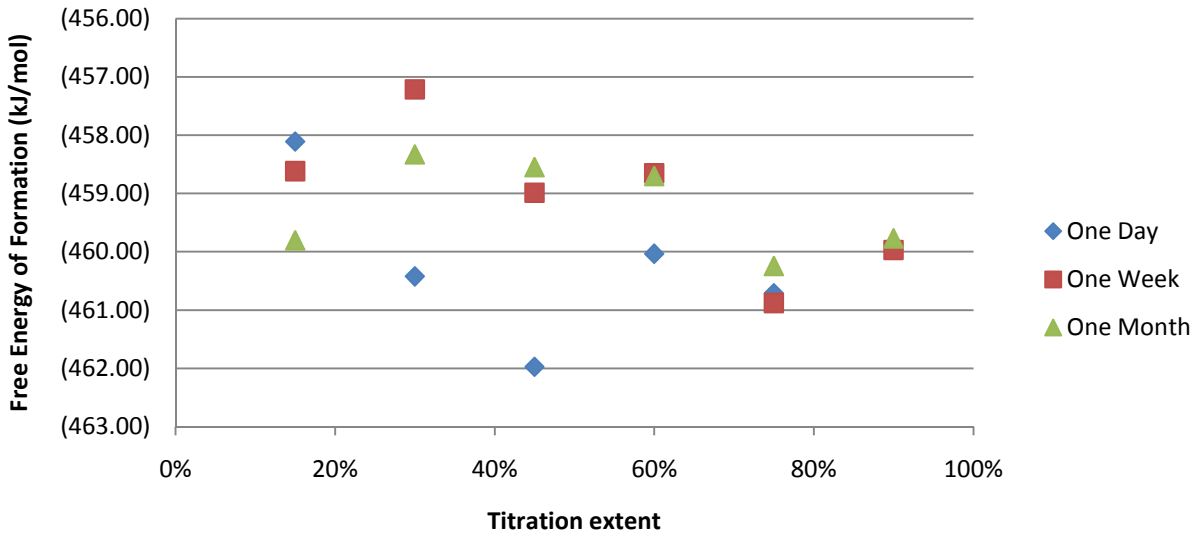


Figure 52 - Calculated free energy of formation of cobalt hydroxide in a mixed nickel and cobalt hydroxide precipitated to various extents from 100 mL of 5 g/L nickel and 0.5 g/L cobalt in sulphate system with 5 mL additions of 22 g/L NaOH, titrated every 30 minutes at room temperature (~22 °C)

Figure 52 shows that unlike all of the other precipitates, the cobalt hydroxide precipitated with nickel hydroxide did not show any significant change in the calculated free energy of formation over time. This may be indicating that when precipitated with nickel, cobalt is stabilised to the solid phase

7. Conclusions

1. Nickel Hydroxide is a separate phase from crystalline nickel hydroxide, with its own free energy of formation

The nickel hydroxide precipitated at room temperature appears to be a gelatinous phase as defined by Stokes and Frith (2008) when in solution. When filtered the gel dehydrates and the aqua molecules forcing the hydroxide gel to remain dispersed are removed, which appears to allow the nickel hydroxide to form a vitreous or glassy state with no long range crystal structure. The free energy of the precipitate was calculated to be -442.0 ±2.5 kJ/mol assuming that each species activity was equal to the respective species concentration. This is greater than the free energy of the crystalline phase given by Bard, Parsons and Jordan (1985) indicating that the gel phase is indeed separate phase from the crystalline nickel hydroxide although the stability of the gel phase is questionable.

2. The nickel hydroxide precipitation formed at room temperature is an enantiotropic (reversible metastable) phase that only occurs under certain temperature conditions

The nickel hydroxide gel is a reversible metastable phase. The gel is less stable than the crystalline phase indicating that it is metastable and its precipitation reaction was reversible.

The nickel hydroxide precipitated at 50 °C was calculated to have approximately the same free energy as that of the room temperature gel, indicating that it too is a non-crystalline metastable phase. Both were also observed to precipitate with a 10-25% hydroxyl deficiency while nickel hydroxide precipitated at 80 °C was observed to precipitate with very little hydroxyl deficiency. The free energy of the 80 °C precipitate was not calculated although one would suspect that it would be much closer to the crystalline due to the lack of hydroxyl deficiency.

3. Nickel hydroxide gel-like precipitate is hydrated and will decompose to a crystalline phase over time

Long term experiments indicated that in the timeframe of one month the free energy of the gel phase was slowly decreasing towards that of the more stable crystalline phase.

Condensation was observed on the lids of the filter cake Petri dishes showing that the cake and therefore the nickel hydroxide precipitate were hydrated. Assuming that the nickel hydroxide was not hydroxyl deficient and that all excess mass in the cake was due to aqua molecules, the

hydration of the freshly filtered nickel hydroxide filter cake was calculated to be 25 aqua molecules per nickel hydroxide molecule. This hydration factor could be even higher if the precipitate was indeed hydroxyl deficient. The hydration of the filter cake was observed to decrease over time. After 4 days it had decreased to 18 aqua molecules per nickel hydroxide molecule. The hydration factor of the nickel hydroxide gel within solution was also calculated to be approximately 220 aqua molecules per nickel hydroxide molecule, based on the same assumptions as the filtered hydroxide.

4. The nickel hydroxide gel-like precipitate forms individual colloidal particles from 1-100 nanometres

Samples of the nickel hydroxide gel were sent to Matec Applied Science in America for particle size analysis on their acoustic sizing equipment but at the time of submission the samples had yet to be analysed.

5. Cobalt hydroxide precipitation carried out at room temperature is very similar to nickel hydroxide precipitation carried out at room temperature

The cobalt hydroxide precipitation was similar to nickel hydroxide precipitation except for a few key points. The cobalt hydroxide precipitated with very little hydroxyl deficiency and over time the cobalt hydroxide gel was observed to decompose over the space of a few days. The cobalt hydroxide was calculated to form with a free energy of -456.5 ±2.5 kJ/mol. As with the nickel hydroxide, this is slightly larger and less stable than the free energy of formation of crystalline cobalt hydroxide as given in literature by Plyasunova, Zhang and Muhammed (1998).

6. Nickel hydroxide stabilises cobalt in the solid phase

Experiments in mixed nickel and cobalt systems clearly showed that the cobalt was indeed stabilised to the solid phase by the presence of nickel or nickel hydroxide. The free energy of cobalt hydroxide formed with nickel hydroxide was calculated to be less, and therefore more stable, than that of cobalt hydroxide precipitated by its self. Furthermore, the individual cobalt precipitate was observed to decompose over the space of a few days while when precipitated with nickel it remained in the gel phase much longer, eventually re-entering the solution within the space of a month rather than decomposing.

7. Cobalt is stabilised in the solid phase by manganese

Experiments in mixed cobalt and manganese systems indicated that the cobalt was in fact stabilising the manganese. When precipitated together the titration curve followed that of the individual cobalt titration curve.

8. The other typical MHP system constituents have a significant effect on the precipitate properties

Cobalt clearly had a major effect on the hydroxide precipitate properties while the presence of manganese and magnesium did not have such a substantial effect. When nickel was precipitated with cobalt the precipitate filter cake was approximately three times the volume of the individual nickel and individual cobalt filter cakes.

When nickel was precipitated with manganese the titration curve followed that of nickel rather than manganese indicating that they precipitated together. The resulting precipitate appeared like a voluminous black gel.

The presence of magnesium did not appear to affect the precipitation or the properties of the gel significantly; even the bright green colour remained.

The presence of cobalt, manganese and magnesium still formed a voluminous gel which eventually changed colour much like the cobalt precipitant.

8. Further Work

A number of areas have where further work is required to prove the unresolved issues from this thesis are:

- XRD analysis on the dehydrated filtrate to prove that it is in an amorphous glassy state
- Particle size analysis on the precipitate in order to confirm the particle size and therefore particle size classification

Some other areas where further work could be directed are:

- Analysis on the gel inclusions is required to gain a greater understanding of the stability of different species within the gel and the attractive and repulsive forces during the formation of the gel
- Investigating the effect of air/liquid and liquid/liquid interface on the precipitation as mentioned by Stoke and Frith (2008)
- Investigating if nickel can be electrowon directly from the gel phase
- Investigating the use of complexing agents to control the nickel concentration within solution and therefore the supersaturation and subsequent primary nucleation of nickel hydroxide
- Investigating the peculiar property of dry nickel hydroxide gel whereby it shatters into shards when submerged in distilled water
- Developing a ternary diagram for the precipitant speciation within a nickel, cobalt and manganese system

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10. Appendices

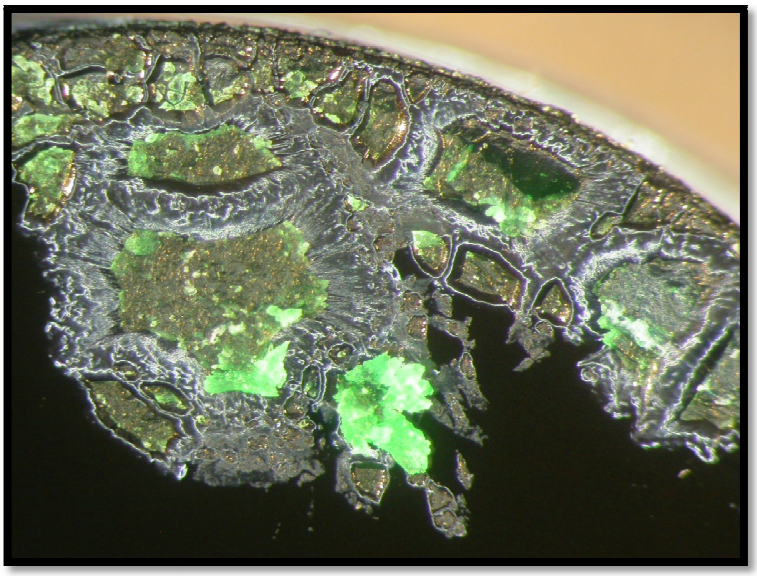
Complete Results Worksheet

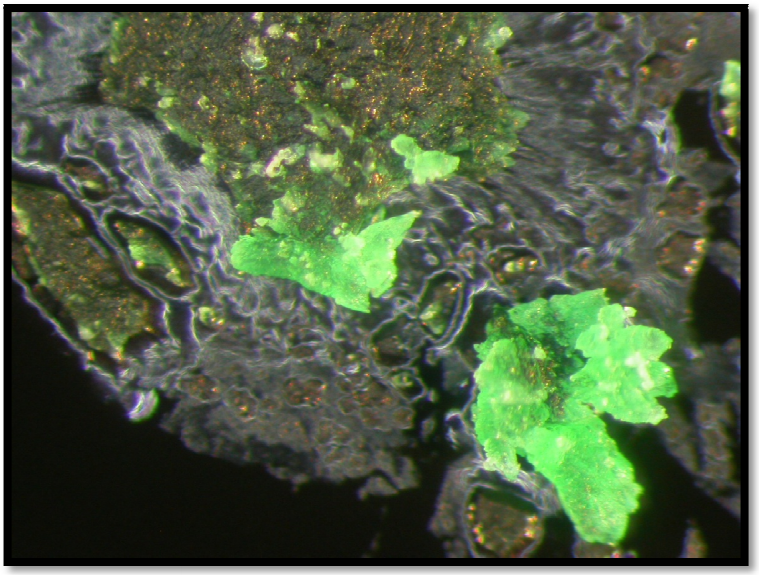
The complete results worksheet has not been included in this report in order to save space. Instead, the Microsoft Office Excel file has been included in the attached CD-Rom.

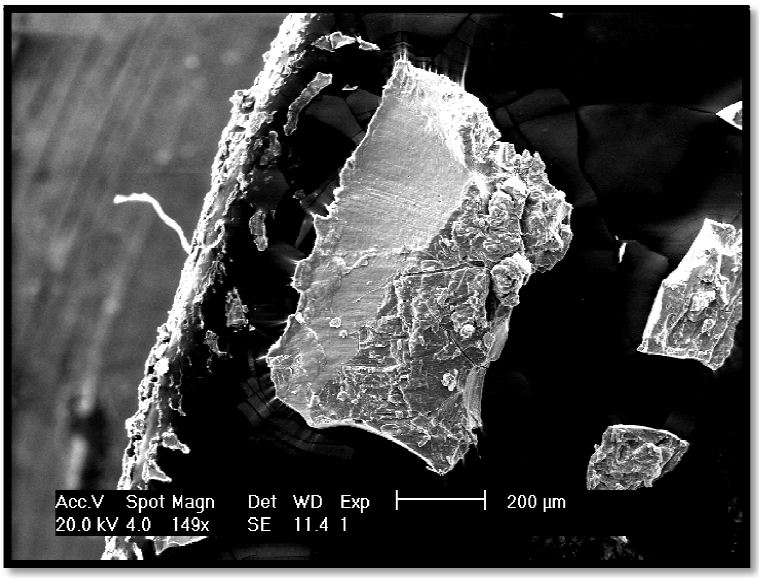
SEM Scoping Analysis

A number of nickel hydroxide precipitation experiments were carried out in the MINE4024 class. These experiments were used to help define the scope and aims of this thesis. Images of the samples under an optical microscope and a SEM are shown. The precipitates put on the SEM stub without being filtered and then were platinum coated in a vacuum which explains the peculiar shrinking patterns visible in the optical microscopy images.

Sample 1 - Nickel precipitated with sodium hydroxide



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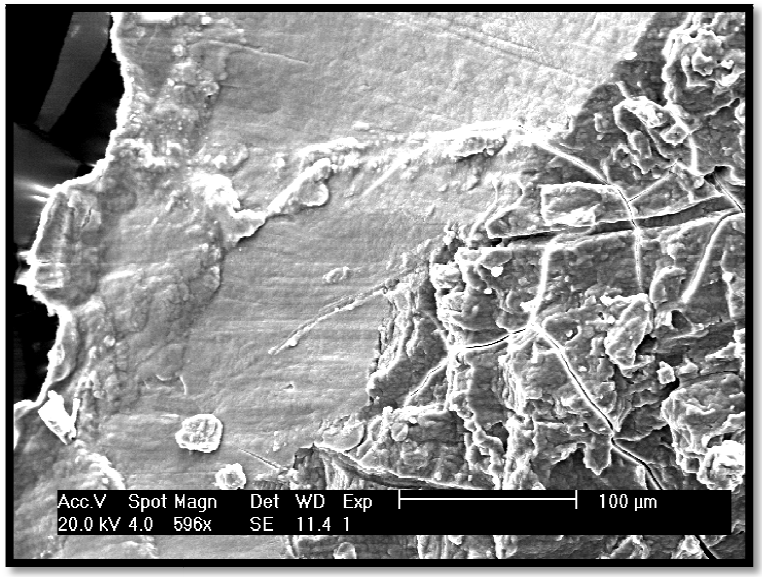
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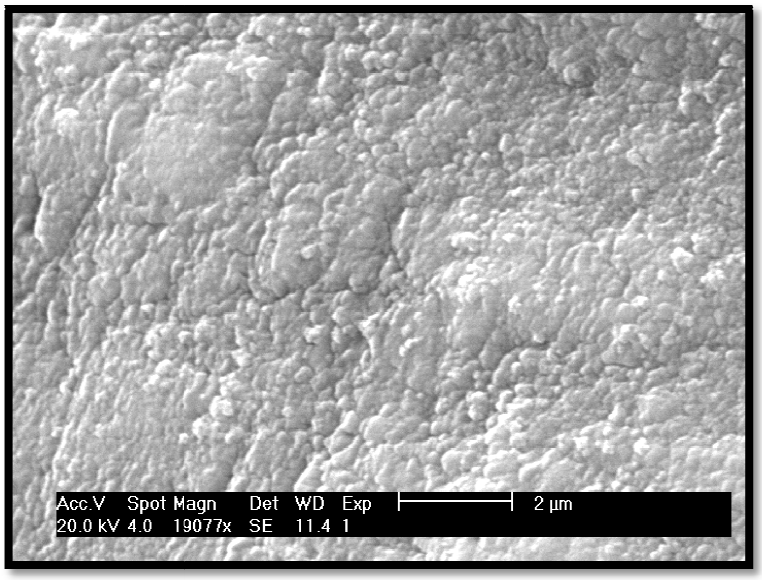
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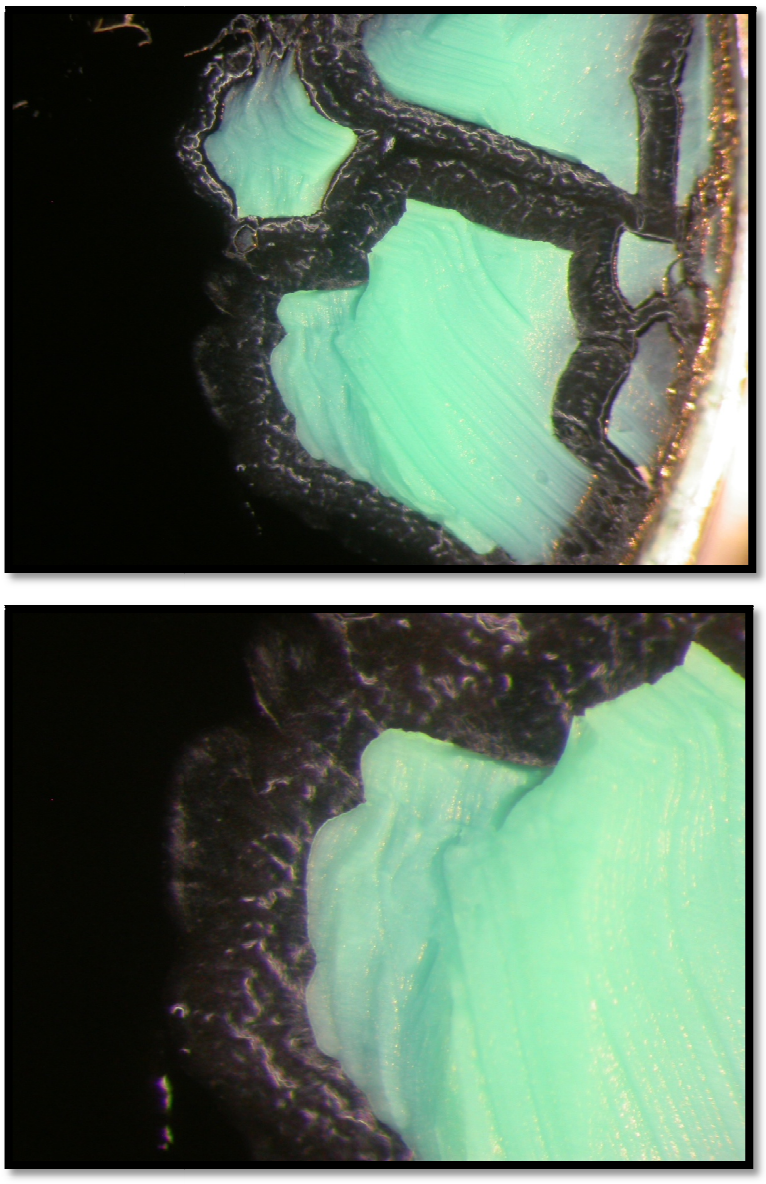

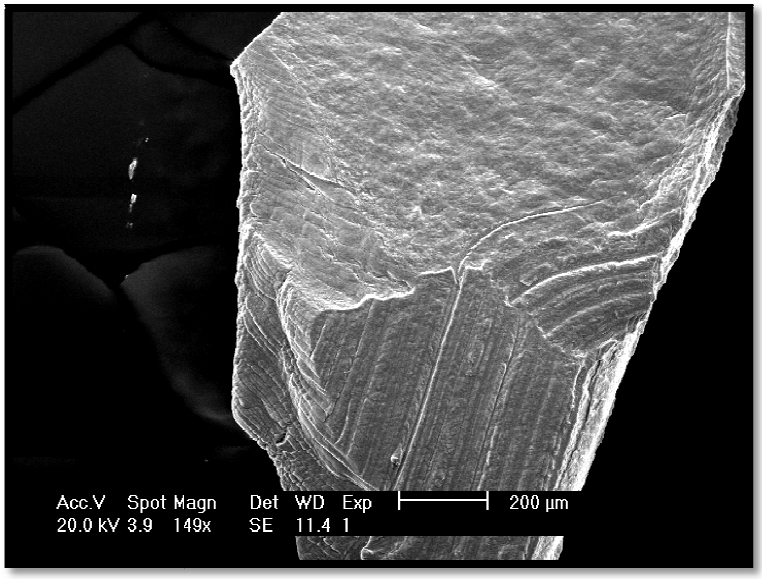
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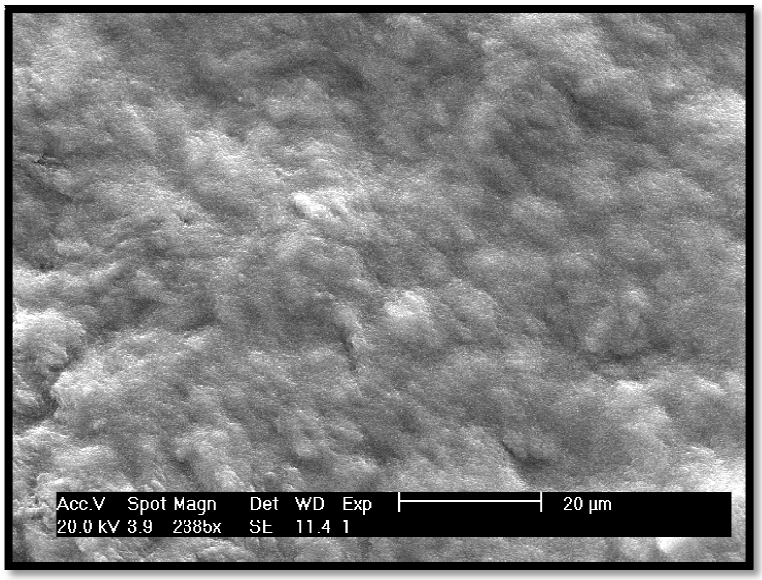
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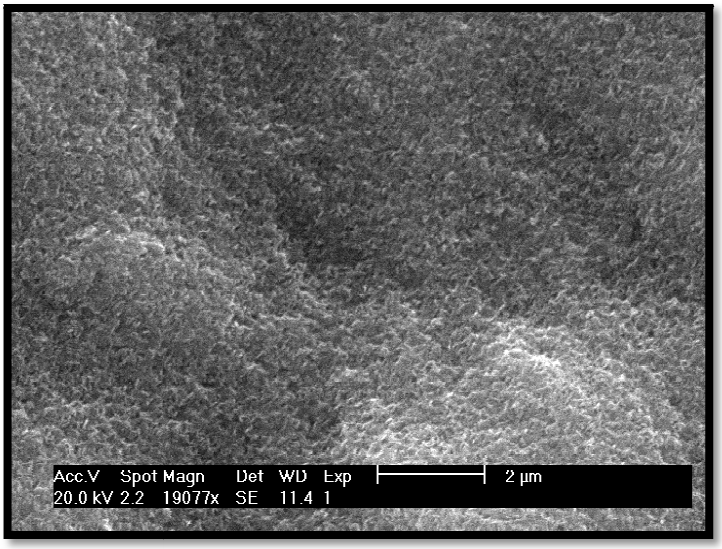
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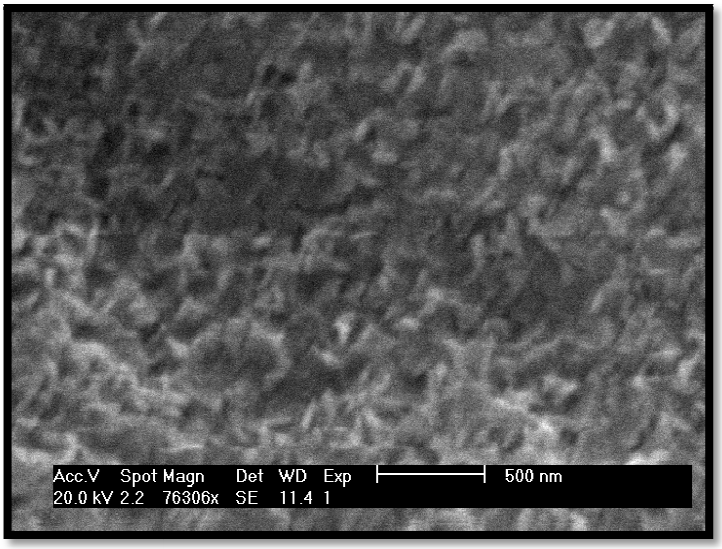
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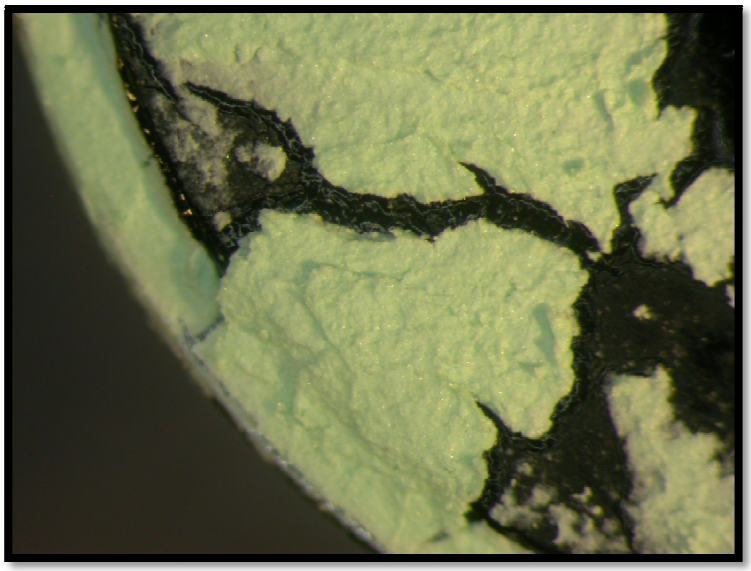
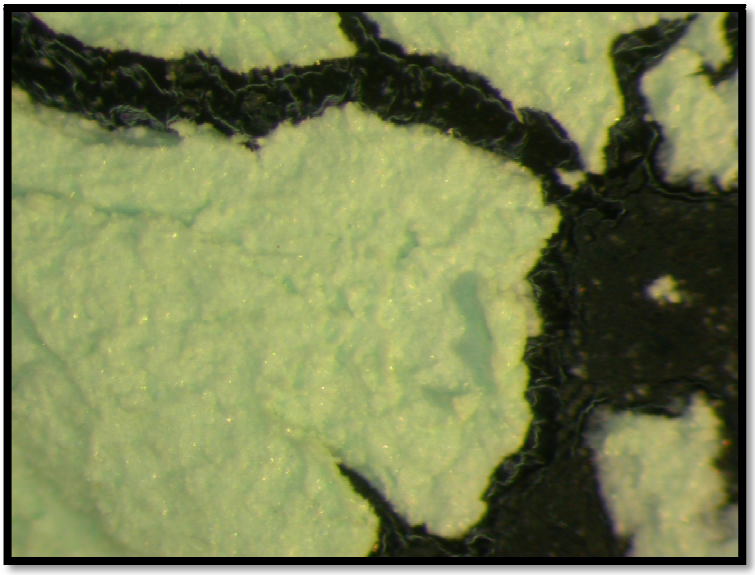
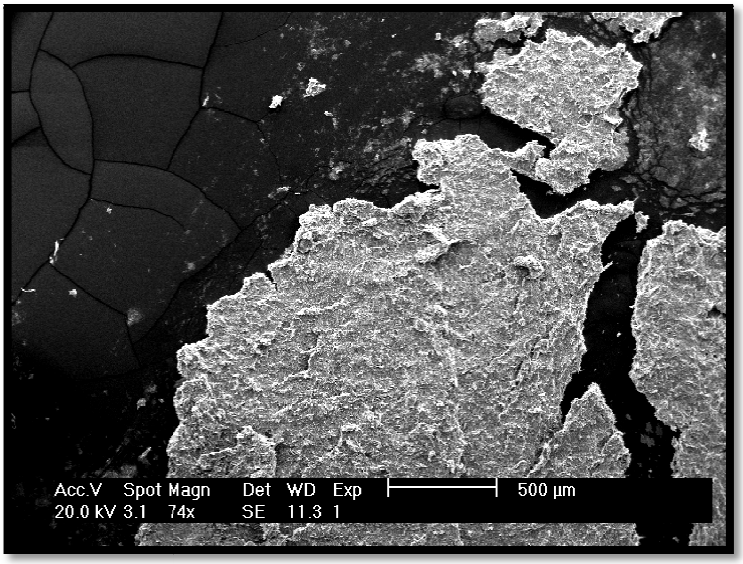
Sample 3 - Nickel precipitated with calcium carbonate slurry



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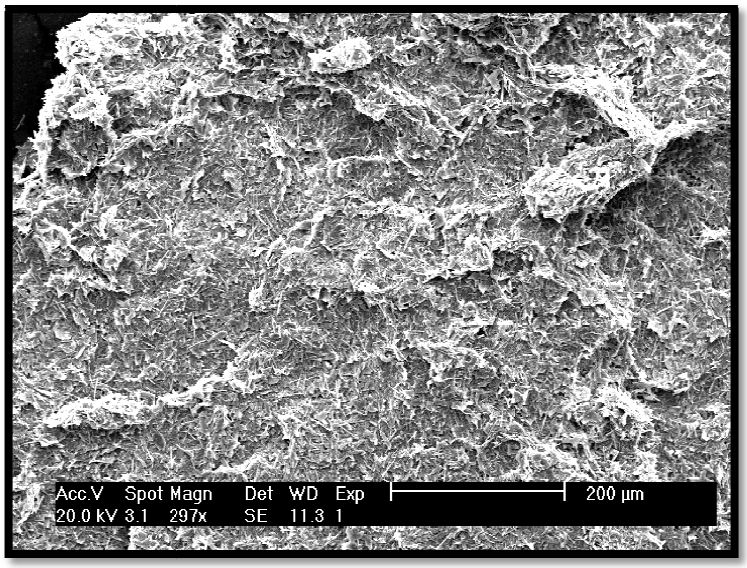
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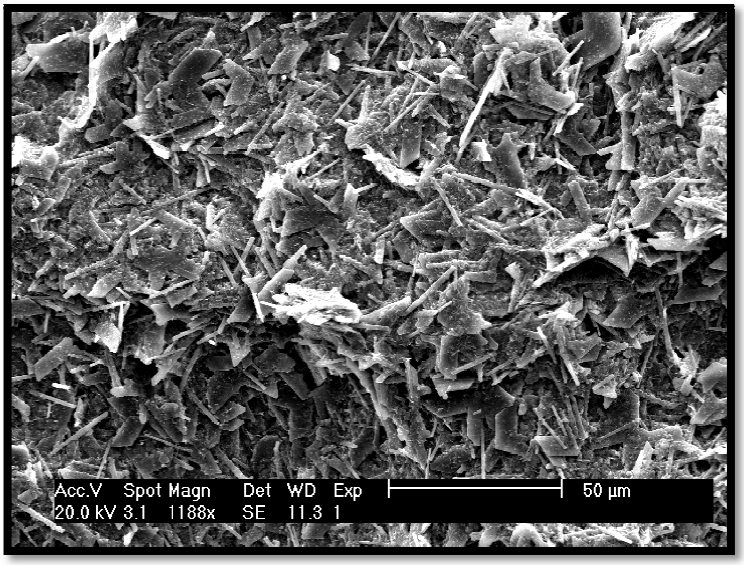
200 µm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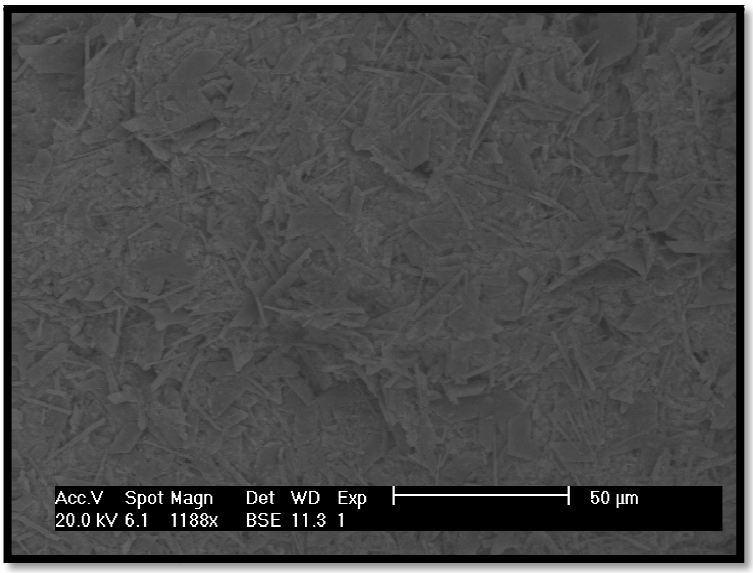
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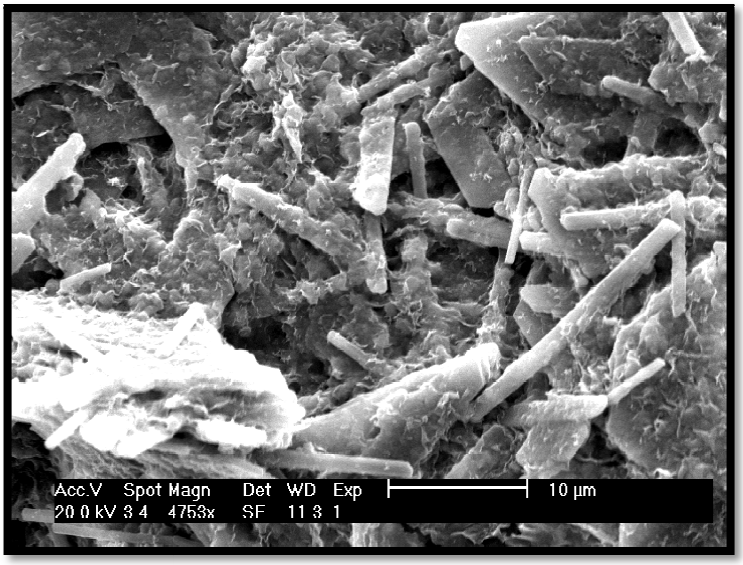
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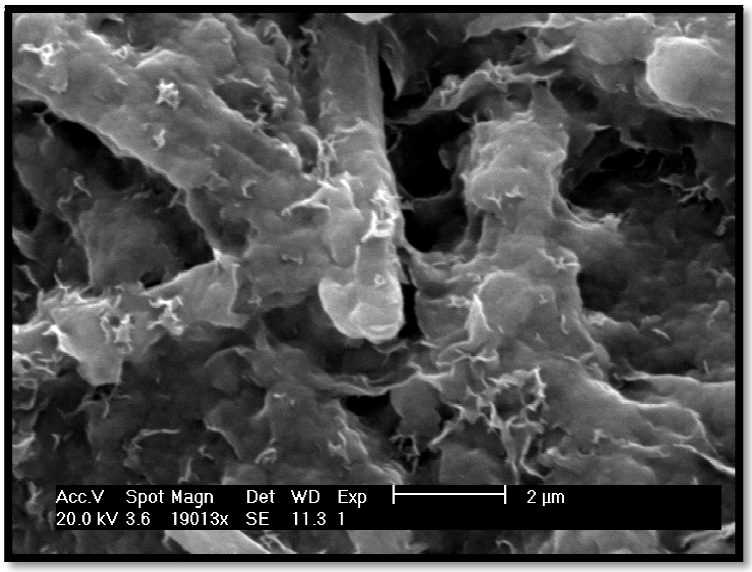
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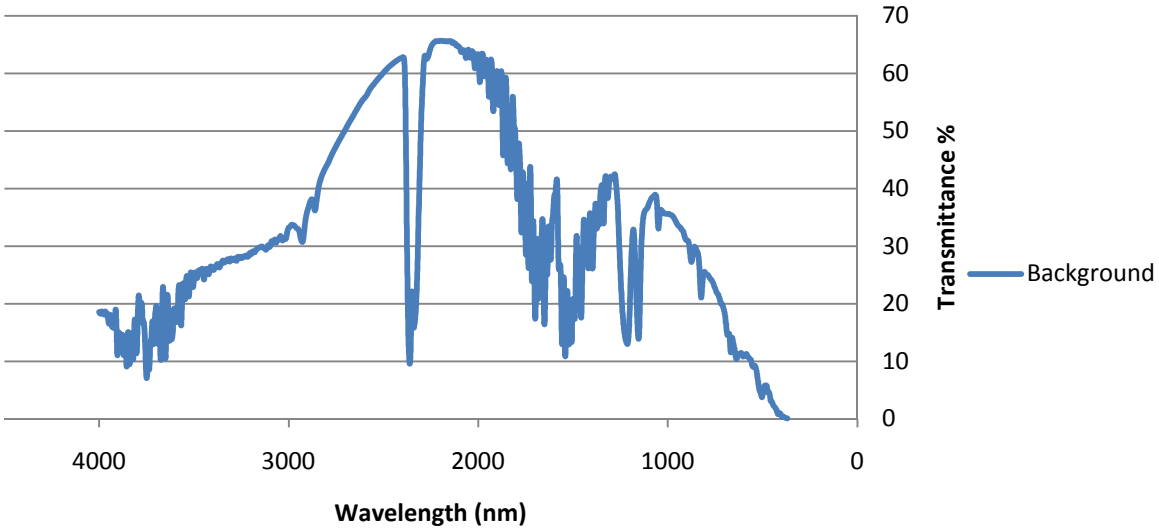
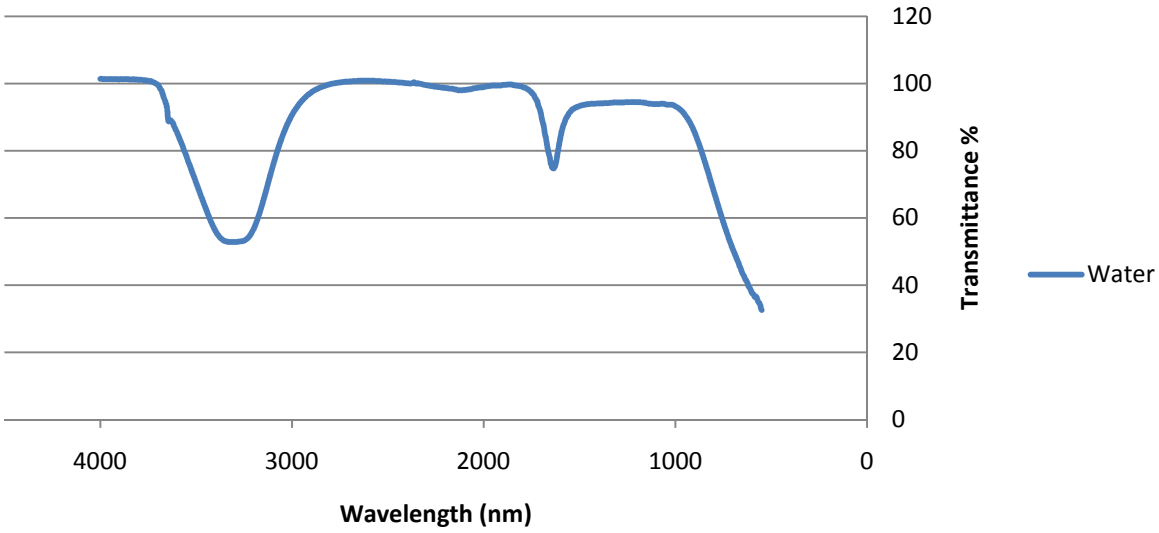
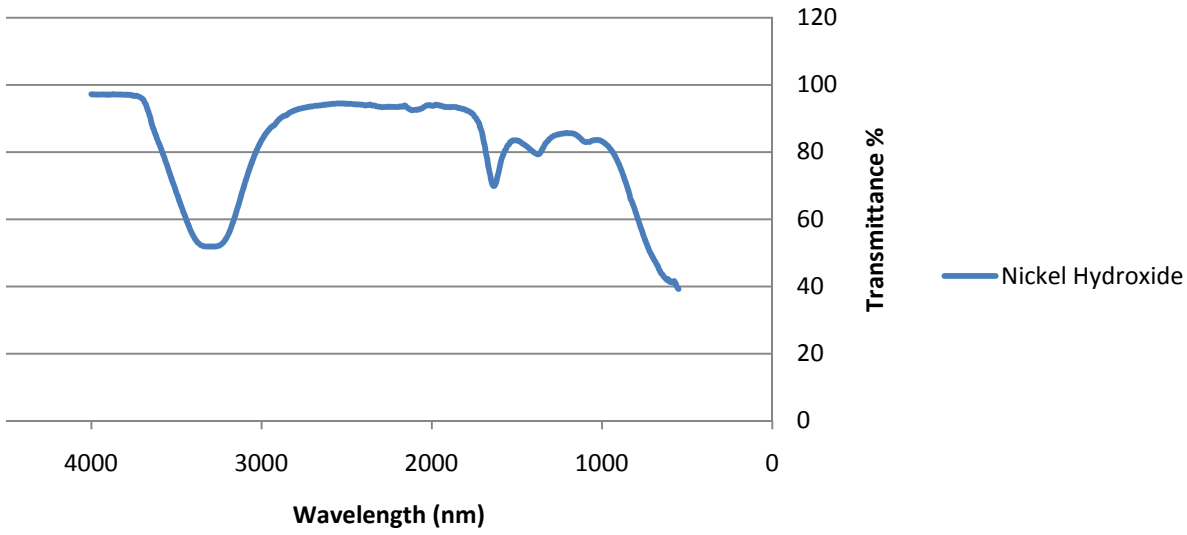
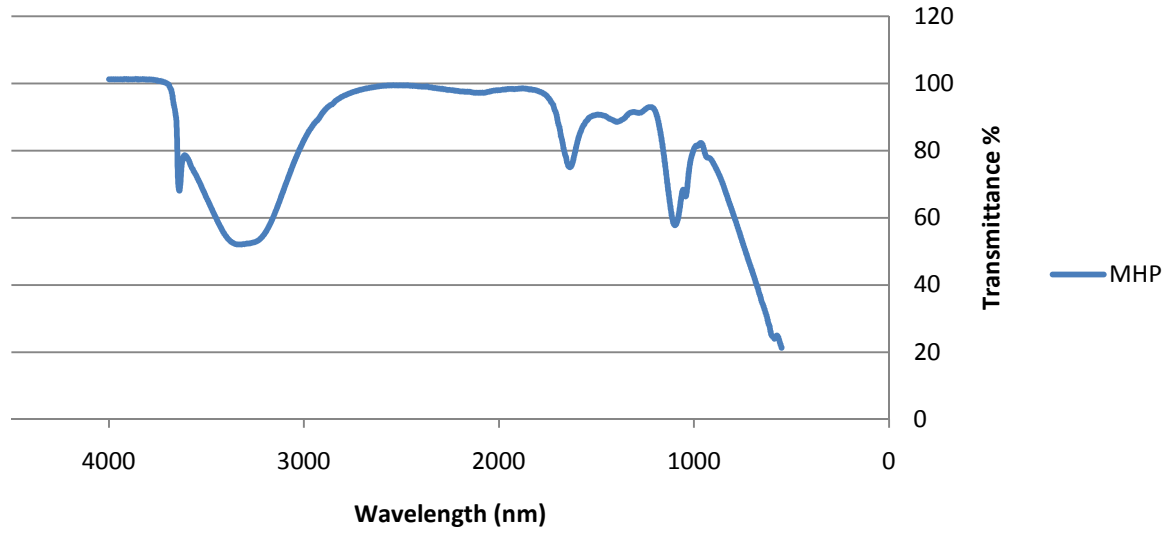
FTIR Scoping Analysis

FTIR analysis was carried out on nickel hydroxide and MHP samples in order to scope the possibility of use in showing the bond types within the precipitated nickel hydroxide.









As the resulting spectra show, the variations in the background and the effects of water in the samples were too high to allow any indication of the nickel or metal hydroxide bonding energies.

Project Risk Assessment

Objective

The objectives of this risk assessment are:

- To plan controls for hazards that can potentially cause harm to myself, others, equipment and the environment
- To plan controls for hazards that can potentially negatively affect the quality and delivery time of the planned thesis deliverables

These controls will be implemented throughout the thesis project in order to reduce all risks to acceptable and manageable levels.

Method

The procedure of risk assessment carried out follows the "Thesis Risk Management Requirements" suggested by Associate Professor Andrew Morrell of the Minerals Safety & Health Centre at the Sustainable Minerals Institute, University of Queensland. The procedure consists of the following steps:

- Process map the thesis at a level that is sufficiently predictable for planning the project's future
- List the potential hazards with each step of the thesis project
- Identify the possible undesirable outcomes that could cause harm to yourself, others, equipment, the environments or adversely affect the thesis for each step
- Establish the risk rank for each hazard by semi-quantitatively assessing both the likelihood that the event could occur and the maximum reasonable consequence of the event using the semi-quantitative likelihood and consequence tables along with the risk ranking matrix
- Sort the potential hazards into descending risk order and establish the level of acceptable risk
- Identify counter measures to ensure all unacceptable risks are controlled in all foreseeable circumstances
- Ensure the required countermeasures are employed effectively to eliminate or mitigate the unacceptable risks

The probability table, shown in Table 1, was used to assess the likelihood of each hazards' occurrence.

Table 1 - Probability Table

Rank	Likelihood	Description
A	Certain	Common occurrence
B	Almost Certain	Expired to occur in most circumstances
C	Likely	Probably will occur or has happened in the past
D	Possible	Could happen at some time
E	Unlikely	Not likely to occur

A typical severity table, shown in Table 2, is used to assess the consequence of each hazard occurrence.

Table 2 - Typical Severity Table

Rank	Consequence	Injury	Property Damage or Process Loss	Environmental Impact
1	Major	Single fatality and/or severe irreversible disability (>30%). (eg fatality of permanently disabling injuries)	Major financial loss ($1M - $10M)	Serious occurrence with some impairment to eco-system. Medium to long term impact.
2	Moderate	Moderate Irreversible disability or impairment	High financial loss	Moderate occurrence not effecting eco-system.

		(<30%). (serious loss time injuries involving loss of limb/or function)	($100,000 - $1M)	Short to medium term impact.
3	Minor	Reversible disability or impairment (eg disabling and short term loss time injuries)	Medium financial loss ($10,000 - $100,000)	Minor Effects. Short term damage to small area.
4	Low	Short term injury (eg medical treatment injuries0	Low financial loss (<$10,000)	No lasting effects. Low level impact. Limited damage to small area.
5	Insignificant	Very low level, short term injury. (minor injuries, first aid injuries or report only)	Minimal financial loss (>$1,000)	Minor spillage. Very low level or nil impact.

The severity table given in Table 3 was developed specifically for thesis projects in mind.

Table 3 - Thesis Specific Severity Table

	Consequence	Thesis Consequence
1	Major	Work time loss/requirement in the order of months (eg redo the work of the last 1 or 2 months) / Quality is majorly affected and the thesis results are virtually useless
2	Moderate	Work time loss/requirement in the order of weeks (eg redo the work of the last 1 or 2 weeks) / Quality is slightly affected and the accuracy of thesis results is affected to the order of ~20-50 percent
3	Minor	Work time loss/requirement in the order of days (eg redo the work of the last 1 or 2 days) / Quality is affected to a minor degree and the accuracy of thesis results is affected to the order of ~5-20 percent
4	Low	Work time loss/requirement in the order of hours (eg redo the work of the last 1 or 2 hours) / Quality is slightly affected and the accuracy of thesis results is affected to the order of ~1-5 percent

5	Insignificant	Work time loss/requirement in the order of minutes (eg redo the work of the last 5 minutes) / Quality is not noticeably affected and the thesis results would not noticeably change

Table 4 was used to quantitatively rank each of the hazards.

Table 4 - Risk Rank Table

Risk Rank		Likelihood				
		A	B	C	D	E
Consequence	1	1	2	4	7	11
	2	3	5	8	12	16
	3	6	9	13	17	20
	4	10	14	18	21	23
	5	15	19	22	24	25

Risk ranks of 20 or above do not require controls as they are deemed acceptable levels of risk, while if a hazard is judged to have a risk rank below 20, controls are required to bring it to an acceptable level of risk.

Results

The thesis process map shown in Figure 1 was developed highlighting the steps required to ensure the project is completed successfully. It also takes into account where problems may arise which result in regression from the project progress and shows how they may affect the progress.

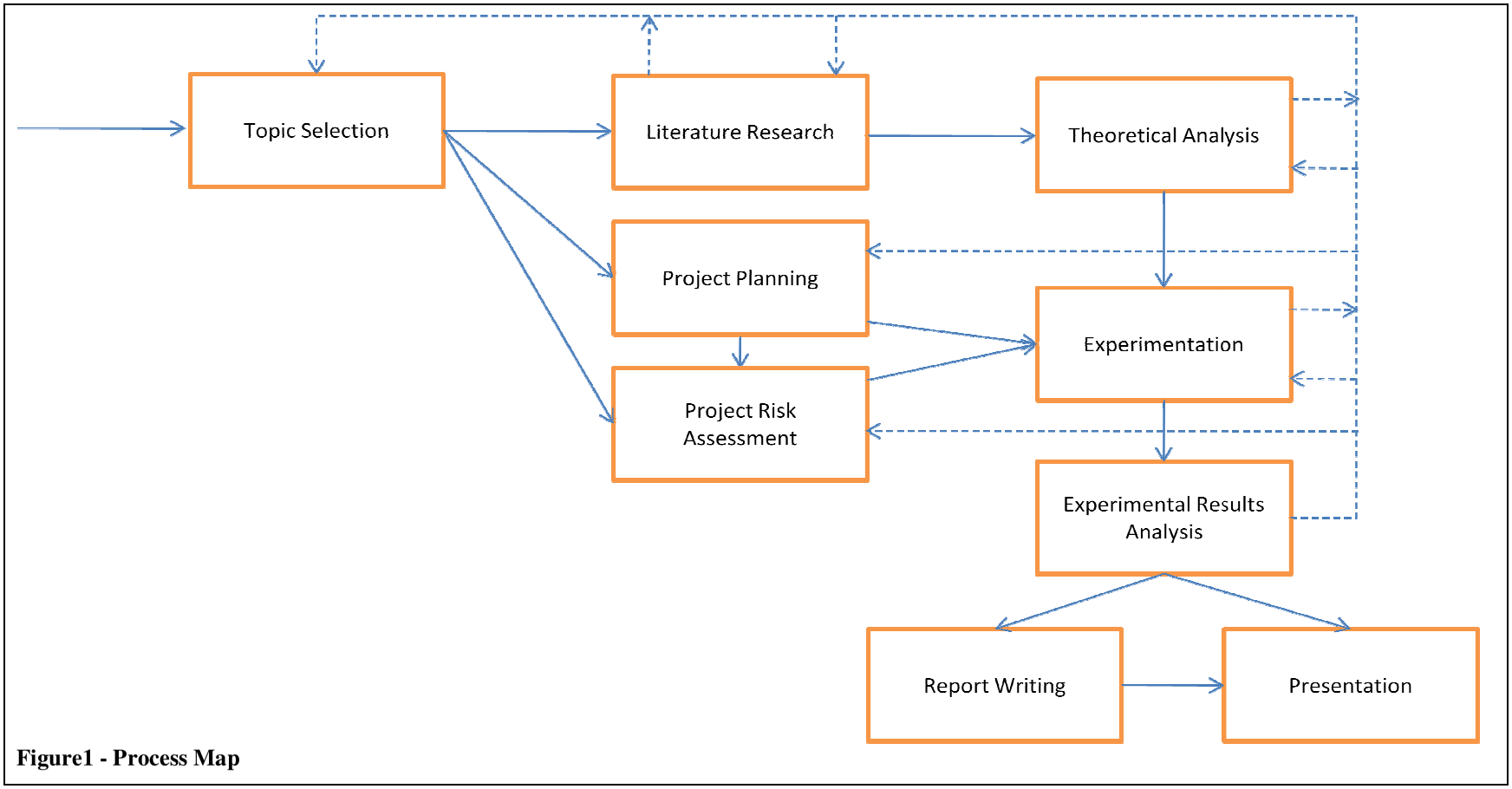


Figure1 - Process Map

The process map presented in Figure 1 was analysed to find the potential hazards. The risk analysis form summarises potential hazards on each project step and the resulting consequence along with the rankings and subsequent controls. This table has been sorted in order of highest to lowest risk rank.

Table 5 - Risk Assessment Form

Thesis Step	Hazard	Maximum Reasonable Unwanted Outcome (Consequence)	**Likelihood of Event**	**Severity of Outcome**	**Risk Rank**	**Control Measures**
Literature Research	Significant literature sources are found late in the project	Major - The thesis will not be comprehensive unless a significant amount of previous work is redone to take the new information into account	B	1	2	- ensure the primary literature search is comprehensive enough to lessen the chance of this occurring while also planning for some time later into the project to take into account any new information by discussing it or choose to completely negate this hazard by ignoring any new information discovered late in the project and dealing with the loss in thesis quality (ignoring the new information is has less

						effect on quality than trying to completely change the thesis work to take it into account)
Project Planning	Incorrect time allocated to tasks	Major - When too much time is allocated, then time will be wasted, while when too little time is allocated then work may not be completed adequately	B	1	2	- periodically reassess the project plan with input from supervisors and using the experience gained on the project to date
Project Planning	Critical path is not identified correctly	Major - Incorrect critical path can lead to holdups while waiting for pieces of equipment etc	C	1	4	- constantly re-assess the project and revaluate long lead time items and potential problems so they can be negated as early as possible, provide bypass options
Project Planning	Required tasks are not identified correctly	Major - The required tasks will have to be completed at some point so they would take up time planned for use on	C	1	4	-periodically reassess the project plan to ensure that it is comprehensive, allow some time in the plan for unforseen tasks

		other tasks				
Project Planning	Deviation from topic and project plan	Major - All off topic work is void and has wasted valuable time	C	1	4	- periodic supervisor meetings to ensure the topic and project plan is followed sufficiently , allow for some deviation from the topic as this may uncover vital discussion points which can be related to the thesis topic
Risk Assessment	Unforseen hazards occur	Major - the uncontrolled energy of the unaccounted for hazard would take effect causing the worst possible consequence for that hazard	C	1	4	- periodically reassess the risk assessment to ensure it is still valid and all hazards are accounted for
Experimentation	Sample contamination	Major - Experimentation results will be wrong but the contamination go unnoticed therefore all thesis results will be	C	1	4	- carry out multiple repeats of each experiment to show repeatability, consistently label all samples and ensure the samples are placed in their

		useless				designated box in the lab whenever they are not being used, cover samples where required
Experimentation Results Analysis	Incorrect interpretation of results and calculation errors	Major - The results will be useless and not applicable to the subject	C	1	4	- Periodic common sense check the calculations, label all data results and test work consistently, use supervisors and theory to check the results
Report Writing	loss of report data	Moderate - The time spent writing the report will have been wasted and the report must be rewritten	B	2	5	- periodic (at least weekly) electronic backups of all thesis work
Choose Topic	Chosen topic is unsuitable for thesis project	Major - All following work will be void until new or modified topic scope and goals are defined	D	1	7	- discuss topic choice with supervisor
Risk Assessment	controls are not	Major - the uncontrolled	D	1	7	- carry out a comprehensive risk

	employed effectively	energy of the hazard would take effect causing the worst possible consequence for that hazard				assessment early in the project and periodically reassess the risk assessment to ensure it is still valid and controls are being employed
Experimentation	Resources are unavailable in the long term weeks/months	Major - Some experiments will not be possible which may require re-evaluation of the topic	D	1	7	- ensure the availability of required equipment with thesis and lab supervisors early in the project
Experimentation	Harmful substance spills/uncontrolled release	Major - Damage to equipment due to uncontrolled releases may mean some experiments are not possible	D	1	7	- complete a job safety analysis for all lab work to identify the required experimental controls
Choose Topic	Topic is interpreted incorrectly	Moderate - All following work will be effected, but may still be applicable, until the topic	C	2	8	- periodic meetings with supervisors to verify the topic scope

		is understood correctly				
Project Planning	Unforseen time sinks eg illness or emergency	Moderate - An illness would result in a few weeks of wasted time	C	2	8	- get a flu injection and allow for some downtime in the planning stages
Theoretical Analysis	Literature information is not understood correctly	Moderate - Theoretical analysis is not possible until the theory is understood	C	2	8	- research a significant amount of background information regarding the thesis topics and discuss with thesis supervisors
Experimentation	incorrect experimental technique used	Moderate - The experimental results will be inaccurate, although results will still be possible	C	2	8	- check with lab supervisors and thesis supervisors as to the correct techniques
Experimentation	Data loss	Moderate - The time spent carrying out the experiment and collecting the data is lost and the experiments will have to be redone	C	2	8	- consistently label all data and periodically backup all electronic thesis data, non electronic thesis data will be kept in the designated box in the lab

Report Writing	writing quality is inadequate	Moderate - The thesis quality will be negatively affected	C	2	8	- use supervisors and other students to gauge the report quality and edit/modify the report until standard is met
Presentation	presentation standard is unacceptable	Moderate - The thesis quality will be negatively affected	C	2	8	- use supervisors and other students to gauge the standard of presentation and edit/modify the presentation until standard is acceptable
Literature Research	ordered papers do not arrive at the library / arrive late	Minor - If the papers arrive late or do not arrive then they cannot be used and other sources must be found	B	3	9	- use other forms of literature and do not rely on the papers
Experimentation	Resources are unavailable in the short term hours/days	Minor - The experiments cannot be carried out in the short term and some valuable time will be lost	B	3	9	- ensure the availability of required equipment with thesis and lab supervisors early in the project
Literature Research	Lack of relevant or credible literature	Major - If no relevant or credible literature can be	E	1	11	- search a wide range of sources and literature types

	found	found then the literature review will be irrelevant to the thesis topic, therefore a new or modified topic will be required				
Experimentation	Designed method of experimentation is not practical	Moderate - a new experimental design is required and resources may need to be ordered to account for this	D	2	12	- check experimental design with thesis and lab supervisors to ensure practicality and edit until it is acceptable
Experimentation	Sample loss	Moderate - Experimentation time was wasted in creating the samples and more time will be required to redo the experiments	D	2	12	- consistently label all samples and place in the designated box in the lab
Experimentation	Injury caused by the experimentation work	Moderate - Chemical burns and eye injuries can occur when using	D	2	12	- complete a job safety analysis for all lab work to identify the required experimental controls

		strong acids and bases				
Experimentation Results Analysis	inconsistent / unreliable results	Moderate - The time spent carrying out the experiment and collecting the data is lost and will have to modify the method and redo the experiments until reliable results are obtained	D	2	12	- carry out multiple repeats of each experiment to validate the results and prove reproducibility
Presentation	loss/malfunction of presentation data	Moderate - The thesis quality will be negatively affected if the malfunction occurs during presentation	D	2	12	- practice and test the presentation to protect against malfunction and always carry electronic backups
Theoretical Analysis	Theoretical calculation errors	Low - The experimental design will be slightly effected by errors in the result but would still be mostly applicable	B	4	14	- carry out sense checking of the results and always consult with thesis supervisors

Conclusions

The project risk assessment carried out for this thesis project provides controls for hazards that can potentially negatively affect the quality and delivery time of the planned project deliverables. The project risk assessment also provides controls for hazards that can potentially cause harm to myself, others, equipment and the environment. This risk assessment follows the procedure suggested by Associate Professor Andrew Morrell whereby a project map is developed and used to spur the detection of hazards. Each hazard is ranked using probability and severity which highlights the hazards which require action.

All of the hazards identified in this project risk assessment were judged to require some form of control. The significant controls required are

- Carry out a very comprehensive literature search taking into account multiple mediums and significant background theory research
- Carry out periodic meetings with supervisors to discuss the project, scope, experiments, experimental technique, results, equipment, work quality and other related items
- Carry out periodic checks on both the project plan and risk assessment to ensure they are both still valid and functioning and modify them if required to take into account any variations
- Carry out repeat experiments to verify accuracy
- Carry out periodic electronic data backups of all thesis work
- Ensure all non electronic work is consistently well labelled and kept in one safe and secure area
- Get a flu injection
- Complete lab specific risk assessments to assess and plan controls for experimental hazards when the experimental design is being developed
- Complete draft reports and presentation and discuss with supervisors

The successful employment of these hazard controls should ensure that a high quality thesis project is completed safely and successfully.